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**TITLE**

PROTOCOL FOR THE CHARACTERIZATION OF EXPLOSIVES-CONTAMINATED SITES

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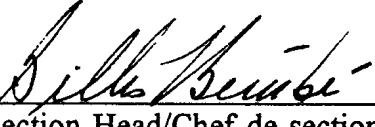
**PROTOCOL FOR THE CHARACTERIZATION  
OF EXPLOSIVES-CONTAMINATED SITES**

**by**

**S. Thiboutot, G. Ampleman and P. Dubé, DREV  
J. Hawari, B. Spencer and L. Paquet, BRI  
T.F. Jenkins and M.E. Walsh, CRREL**

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**Approved by/approuvé par**

  
\_\_\_\_\_  
**Section Head/Chef de section**

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ABSTRACT

Many activities of the Canadian Forces, such as firing, demolition procedures and destruction of obsolete ammunition by open burning and open detonation may lead to the dispersion of energetic compounds in the environment. These compounds are being closely examined due to their highly specific physical, chemical and toxicological properties. In Canada, limited effort has been devoted to examine this particular environmental threat. In this context, R&D was dedicated towards the establishment of a protocol that will allow reliable and safe characterization of sites potentially contaminated with explosives. This protocol was based on Defence Research Establishment Valcartier (DREV) research efforts and expertise in the chemistry of energetic materials, on the current existing literature, on the experience gained in practical field sampling and on collaborative work with BRI and CRREL. The protocol detailed in the present report covers all aspects related to surface and subsurface sampling, extraction, analysis, field-screening methods and environmental fate related with these specific contaminants. Furthermore, safety procedures are described that take into account the explosive and toxic nature of these compounds. This protocol will serve as a reference guide for future sampling campaigns on sites that are potentially contaminated with explosives.

RÉSUMÉ

Plusieurs activités des Forces canadiennes comme le tir, les pratiques de démolition et la destruction de munitions désuètes par incinération et par détonation peuvent mener à une dispersion de composés énergétiques dans l'environnement. Ces composés pourraient représenter une gamme de contaminants pour l'environnement. De plus, ils ont des propriétés bien particulières du point de vue physique, chimique et toxicologique. Au Canada, rien n'a été entrepris par le passé pour examiner cette menace environnementale. Dans ce contexte, des études de R&D ont permis la création d'un protocole qui permettra la caractérisation fiable et sécuritaire de sites potentiellement contaminés par des explosifs. Ce protocole est fondé sur une solide expertise du CRDV au niveau de la chimie des matériaux énergétiques, sur la littérature existante, sur l'expérience pratique acquise lors d'échantillonages et grâce à des collaborations établies avec l'IRB et le CRREL. Le présent rapport est détaillé et couvre tous les aspects reliés à l'échantillonage souterrain et en surface, à l'extraction, à l'analyse, aux méthodes d'analyse de terrain et au transport environnemental de ces contaminants particuliers. Par ailleurs, les procédures de sécurité décrivent tiennent compte du comportement explosif et toxique de ces composés. Ce protocole servira dans le futur de référence pour l'échantillonage de terrains potentiellement contaminés par des composés énergétiques.



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EXECUTIVE SUMMARY

It is a goal of the Department of National Defence (DND) to implement environmentally benign defence activities. This involves scrutinizing all defence activities to ensure that they have no adverse impact on the surrounding environment. It is within this context, and also within the context of base closures and demilitarization, that the Defence Research Establishment Valcartier (DREV) initiated five years ago an R&D program to study the environmental impacts of energetic materials, specifically those that are to be found in the CF ammunition stockpile. Activities such as firing exercises, demolition procedures and destruction of out-of-specification ammunition can lead to the dispersion of energetic compounds in the environment.

Energetic compounds are just now being recognized as environmental contaminants compared to other contaminants such as petroleum or solvents. They are also unique of concern, because of their specific chemical, physical and toxicological properties. Thus, a protocol for the effective characterization of sites potentially contaminated by these compounds has to be written. DREV has developed an expertise in energetic compounds over the past few years by implementing the necessary analytical chemistry, reviewing all pertinent literature, establishing international collaborations, studying field techniques unique to energetic materials and sampling many CF ranges. This expertise gained within all these activities has led to the establishment of a detailed sampling protocol which describes all necessary aspects for the effective and reliable characterization of explosively contaminated sites. The present protocol will serve as a reference guide for future sampling and characterization of CF ranges for the determination of the extent of contamination of soils and groundwater by energetic compounds. The characterization of training, demolition and open burning/open demolition ranges will help the DND to assess the environmental impacts of these activities and will provide critical information to establish future operational requirements and procedures. DREV has already studied and characterized several DND sites, and has built up a database that has proven to be helpful both to establish the present protocol and to advise DND authorities of the probable environmental effects of CF activities either on-going or under consideration.

Another aspect of DREV's R&D program is the development of practical and economical remediation technologies for the cleaning of explosive-contaminated sites. Both programs on soil characterization and soil remediation will position the DND in a state of readiness for any future potential contamination problems. The remediation aspect will not be discussed in the present report but will be covered in future documents.



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NOMENCLATURE

ACN	Acetonitrile
2-ADNT	2-amino-4,6-dinitrotoluene
4-ADNT	4-amino-2,6-dinitrotoluene
ANOVA	Analysis of variance
AP	Ammonium perchlorate
ASE	Accelerated solvent extractor
BRI	Biotechnology Research Institute
CF	Canadian Forces
CRREL	Cold Regions Research and Engineering Laboratory
2,4-DANT	2,4-diamino-6-nitrotoluene
2,6-DANT	2,6-diamino-4-nitrotoluene
DNB	Dinitrobenzene
DND	Department of National Defence
DREV	Defence Research Establishment Valcartier
2,4-DNT	2,4-Dinitrotoluene
2,6-DNT	2,6-Dinitrotoluene
EIA	Enzyme immunoassay
FAC	Field analytical chemistry
GC	Gas chromatography
HMX	Cyclo 1,3,5,7-tetramethylene-2,4,6,8 tetranitramine
HPLC	High pressure liquid chromatography
MHT	Maximum holding time
MS	Mass spectrometry
NB	Nitrobenzene
NC	Nitrocellulose
NG	Nitroglycerine
nm	Nanometer
NQ	Nitroguanidine
2-NT, 3-NT, 4-NT	2-nitrotoluene, 3-nitrotoluene, 4-nitrotoluene
OB/OD	Open burning/open detonation
PBX	Plastic-bonded explosive
PTFE	Polytetrafluoroethylene
PVC	Polyvinyl chloride
RDX	Cyclo-1,3,5-trimethylene-2,4,6-trinitramine
R&D	Research and Development
SFE	Supercritical fluid extraction
SPME	Solid phase microextraction
2,4,6 TAT	2,4,6-triaminotoluene
Tetryl	2,4,6-Trinitro-phenylmethylnitramine
TNB	Trinitrobenzene
TNT	Trinitrotoluene
WES	Waterways Experiment Station



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1.0 INTRODUCTION

Identifying and developing economical and effective methods to eliminate undesirable contaminants from soil and groundwater is of worldwide growing environmental interest and importance. The task is all-the-more critical and complicated when the contaminants are energetic materials, which are the main components of gun powders, explosives warheads and solid rocket propellants. The new international context with the end of the Cold War has resulted in the closing of many military bases and a growing awareness in environmental issues. This awareness has led many countries to integrate R&D programs related to the environmental impacts of energetic materials. It is within this context that the Canadian Defence Research and Development Branch has directed some of its resources to assess the environmental risks associated with explosive compounds.

Many Canadian Forces sites such as impact areas, training ranges, demolition and open burning/open detonation (OB/OD) ranges, which are used to destroy the out-of specification materials, are highly suspected of being contaminated by energetic substances, as described in the literature (Refs. 1-6). Explosive manufacturing sites could also be contaminated with energetic compounds. In order to evaluate the potential contamination of DND sites, the sampling and characterization of various types of ranges have been performed in the last four years. All standard sampling, analysis and data management techniques should be applied (Refs. 7,8) when characterizing explosive-contaminated sites. However, the overall work within this task has led to the establishment of a specific sampling protocol which addresses different aspects related to these new crystalline organic contaminants.

The term explosive is commonly used to refer to propellants, explosives and pyrotechnics which typically fall into the more general category of energetic materials. Figure 1 outlines the various categories of energetic materials.

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Propellants include both rocket and gun propellants. Most rocket propellants are based on a rubber binder, on ammonium perchlorate (AP) oxidizer and they might also contain powdered aluminium fuel. Some are also based on a nitrate ester, usually nitroglycerine, (NG) nitrocellulose (NC) and cyclo 1,3,5,7-tetramethylene-2,4,6,8 tetranitramine (HMX). Gun propellants usually are single based (NC), double based (NC and NG) or triple based (NC,NG and nitroguanidine (NQ)). Some of the newer, lower vulnerability propellants contain binders and crystalline explosives.

Pyrotechnics include illuminating flares, signalling flares, coloured and white-smoke generators, tracers, incendiary delays, fuzzes and photo-flash compounds. Flares are composed of an inorganic oxidizer and metal powder in a binder. Illuminating flares contain sodium nitrate, magnesium, and a binder. Signalling flares contain barium, strontium, or other metal nitrates. Smoke generators are mainly composed of red and white phosphorous and coloured smoke also contains organic colorants.

Explosives are classified as primary or secondary based on their susceptibility to initiation. Primary explosives, which include lead azide and lead styphnate, are highly susceptible to ignition. Primary explosives are often referred to as initiating explosives, because they can be used to ignite secondary explosives. Secondary explosives, which include trinitrotoluene (TNT), cyclo-1,3,5-trimethylene-2,4,6-trinitramine or research development explosive (RDX), cyclo-1,3,5,7-tetramethylene-2,4,6,8 tetranitramine or high melting explosive (HMX) and 2,4,6-trinitro-phenylmethylnitramine or tetryl, are much more prevalent on military sites than are the primary explosives. Since they are formulated to detonate under specific circumstances, secondary explosives often are used as main charge or boosting explosives. They can be categorized into melt-cast explosives, which are based mainly on TNT, and plastic-bonded explosives (PBX), which are based on a binder and a crystalline explosive such as RDX. Secondary explosives can also be classified according to their chemical structure as nitroaromatics which includes TNT, and nitramines, which include RDX and HMX. Figure 2 shows the chemical

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structure of common explosive compounds, while Table I (Ref. 9) present the physical and chemical properties of nitroaromatics, and nitramines.

Many chemicals included in energetic formulations could be found as soil and groundwater contaminants since they are leaching mobile contaminants which can migrate with rainfall through groundwater. Energetic materials composing propellants are either polymeric substances (NC) or nitrate esters such as NG. Those contaminants will be further addressed when future R&D work will be carried out on the sampling and characterization of those particular compounds. On the other hand, pyrotechnics are mainly based on chemicals for which sampling and analytical methods already exist. Furthermore, the phosphorous based flares will lead to phosphates in the environment and this does not represent a threat when these flares are used in dry soil. However, when phosphorous-based materials are dispersed in a wetland environment, it represents a serious threat since phosphorous stays as an element. This is not the case for any Canadian site, while some wetlands in the United States are contaminated with phosphorous.

Our efforts were first targeted at the characterization of secondary explosive compounds in soil and groundwater, since they represent the major threat. Thus, DREV worked on establishing a sampling procedure specific to explosive compounds such as TNT, RDX and HMX. TNT and RDX are major ingredients in nearly every munition formulation and are the secondary explosives used in the largest quantities (Ref. 9). Several other organic chemical explosives have also been used in specific munition formulations, including 2,4-dinitrotoluene (2,4-DNT), HMX, tetryl and trinitrobenzene (TNB). While some of these chemicals, such as tetryl, are no longer used in current munitions, residues from their manufacture and use remain at contaminated sites. In addition to chemicals added to explosive formulas, munition residues often contain other chemicals resulting from impurities in production or as environmental transformation by-products. For example, military grade TNT often contains a number of impurities, including 2,4-DNT and other isomers of dinitrotoluene. In addition, TNT is highly

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subject to photo and microbial degradation from which a variety of transformation products have been identified (Ref. 9). The major impurity in production grade RDX is HMX, which can be present at concentrations as high as 12% (Ref. 10). The extraction and characterization protocol must include all these co-contaminants and has to take into account the sensitive nature of these molecules towards biotic and abiotic transformations.

The present report represents a guide for any CFB environmental officer who might plan to characterize potentially explosive-contaminated sites. It will also serve as a reference tool for the contractors who will carry out the characterization work. The report will describe all aspects related to sampling, extraction, analysis, environmental fate and safety when characterizing sites. Furthermore, this report can be viewed as a literature survey since it refers to many papers in which more detailed information can be found on each topic.

This work was carried out at DREV between September 1995 and August 1997 under WU 2ef11, Characterization of DND Sites Contaminated with Energetic Materials and was sponsored by a task coming from Directorate General Environment (DGE) through the Directorate of Ammunition Program Management (DAPM). A part of this work was done in collaboration with Cold Regions Research and Engineering Laboratory (CRREL) and Biotechnology Research Institute (BRI) scientists.

**2.0 SAMPLING**

The accurate chemical characterization of a hazardous waste site requires the development and implementation of a well-designed sampling plan. After defining the area of interest, which might be an entire site or several defined areas within a site, samples are collected according to one or several possible schemes. The distribution of contaminants is very site specific, depending on the manner in which the contamination occurred, the physical and chemical properties of the contaminant involved, soil type, and the geology and hydrogeology of the site.

The particular nature of explosives as contaminants must be taken into consideration for all aspects related to the sampling, conservation and analysis of soil or water matrices. Explosives are solid at ambient temperature; they dissolve slowly and sparingly in aqueous solution and have low vapour pressure (Table I). These properties limit their mobility compared to other organic contaminants such as fuel or solvents. These specific contaminants demonstrate a pattern of high degree of heterogeneity in their spreading because of their low solubility and their crystalline nature. A protocol that will minimize this heterogeneous waste distribution must be implemented and the use of field screening methods is of high value since it will help to establish a sampling pattern and reduce laboratory analytical costs. The sampling of soil and groundwater and conservation of these samples must also take into account the particular nature of those relatively new contaminants.

This chapter will cover surface soil sampling and groundwater sampling. Since explosives demonstrate a low water solubility, the probability of finding high levels of explosives directly on or near the surface is high, even for sites that have remained dormant for many years. This, of course, will depend on the specific target explosive and will also depend on the nature of the soil matrix. In any cases, subsurface soil sampling is needed to characterize the contamination plume and also to reach the watertable. This will be discussed in Chapter 4.

## 2.1 Soil Sampling

A minimum of 500 g of soil must be sampled for each discrete or composite sample. Explosives are not volatile compounds (see Table I) and therefore, no specific precautions such as the use of sealed containers must be taken. The containers that are recommended for use are 1-litre amber glass bottles with a polypropylene or black phenolic baked polypropylene cap. Amber glass should be used in order to prevent the photodegradation of light-sensitive TNT and TNT derivatives. However, polyethylene bags might be used since this material is resistant to absorption of explosives when used

in conjunction with relatively dry soil samples. The bags must be immediately stored in ice coolers in the dark. The use of polyethylene bags decreases the space needed for storing samples, reduces shipping costs and has lower risks associated with the transport of samples. As it will be discussed in Section 2.5, the samples must be kept at low temperatures from the time of collection until the analytical work is completed.

## 2.2 Spatial Heterogeneity

Several papers have been published by CRREL scientists on the subject of short-range spatial heterogeneity of explosive concentrations in surface soils (Refs. 11-12). They have extensively studied the spatial heterogeneity distribution pattern of various explosives on different ammunition plants in the U.S. Table II provides information on the detection of explosive residues in soils analyzed by CRREL and another laboratory of the Corps of Engineers (Ref. 13). CRREL scientists have sampled many sites and studied the spatial distribution of TNT (Ref. 11) and other explosives such as ammonium picrate (Ref. 12). A collaborative study between CRREL and DREV has also led to the study of spatial heterogeneity of explosive compounds at an HMX contaminated site (Refs. 14-16).

Initial sampling campaign (Refs. 11-12) were conducted using a common pattern for all sampled locations. Briefly, the sampling pattern is based on the use of a plastic template that is placed on the ground with the centre of the template placed in the recommended sampling location. Seven discrete samples are collected in a circular pattern with the first sample taken from the centre (Fig. 3). The radius of the wheel is 61 cm and the samples are taken around the arc of the wheel at 61-cm intervals. Samples are collected on the surface from 0 to 15 cm depth using a manual stainless steel hand auger. The seven discrete samples are collected first and then composite samples are built. In general, the composite samples are built by subsampling the soil remaining after discrete sampling and the seven grab samples are combined and homogenized by hand mixing. The material is conned and quartered. About 5-g samples are removed from

each quarter and combined to produce a 20-g sample for field analysis. Field replicates of the discrete and composite samples are collected in order to study the reproducibility.

Statistical analyses of the overall results of the sampling events were conducted for both the field and lab results. These statistical analyses were conducted to study the significant concentration differences among the sample positions at each sampling location. The analytical results of both methods of analysis were subjected to one variable of classification, completely randomized analysis of variance (ANOVA). The details of the statistical analyses method can be found in Refs. 11-12. All sites sampled showed that absolute variance for the seven discrete samples were heterogenous. Furthermore, all the results showed that the sampling error exceeded the analytical error by an order of magnitude. The results also demonstrated that the homogenization of discrete samples and combination to form composite samples leads to the minimization of the characterization problems caused by heterogeneity dispersion.

The large short-range spatial heterogeneity of explosive concentrations in surface soils was found to be significant, regardless of whether the major contaminant was TNT, 2,4-DNT or ammonium picrate. Extreme spatial heterogeneity was found in samples separated by only 60 to 120 cm. Ratios of the highest to the lowest concentration, for a group of seven samples ranged from about 3 to greater than 600, with a median value of 50. However, composite sampling coupled with on-site analysis offers a mean to obtain more reliable and representative results.

The short and medium-range heterogeneity of HMX dispersion pattern was studied by the characterization of the spatial distribution of HMX on an active anti-tank firing range (Refs. 14-16). On this particular sampling campaign, a combination of "area integrated sampling", in field samples homogenization, compositing to produce representative grid samples, and on-site analysis were used. The depth of contamination and the dimensions of the sampling grids were determined by using on-site methods. The

seven discrete sample pattern was also applied to compare the heterogeneous nature of HMX dispersion with other previously explosive dispersions.

The major objectives of this work was to further characterize the short-range spatial heterogeneity of contaminants in near the surface soil, and to develop a sampling strategy that would provide representative samples. To overcome heterogeneity problems, a combination of collecting an area-integrated sample and a simple compositing approach within defined geographic (grid) boundaries was studied.

To assess larger-scale heterogeneity on this site, the area between two tanks targets was divided into fourteen 6 m x 6 m grids, then each grid was subdivided into four 3 m x 3 m subgrids. The samples within each subgrid were obtained as follows: A spading shovel was used to scrape the top 5 cm of soil from a circle of medium radius of 77 cm in the centre of each subgrid (Fig. 4). The soil scraped from the surface was piled in the centre of the circle and mixed thoroughly with the spading shovel and a small hand shovel. Pieces of metallic and ceramic debris from munition detonation were removed by hand and a subsample of about 1 kg of soil was collected from random locations in the pile. Duplicate portions of soil from these soil piles were collected in nine randomly selected subgrids. In these same nine subgrids, a duplicate was prepared from a separate sampling circle in the subgrid, in a manner identical to that described above except that the sampled area was offset from the initial one. These samples were labelled "area integrated" since they represented the entire sampled circular area. Weighed portions from each of the four area integrated subgrid samples from within a grid were combined and homogenized in duplicate to prepare two composite samples to represent each grid.

A statistical analysis was again conducted on the analytical results that were obtained. The concentration estimates for the grid composites were generally within 25% of the mean of the four subgrid samples. Thus it was possible to prepare composite samples in the field that accurately represented the mean of the discrete samples. By comparing the reproducibility of discrete grab samples with area integrated subgrid

samples, it was obvious that the second approach led to a much improved ability to obtain reproducible samples. Again, this sampling campaign highlighted the fact that the sampling error greatly exceeds the analytical error, and that the homogenization and compositing approach minimize the sampling error. Thus, a characterization campaign of the explosive-contaminated sites should involve the collection of composite samples and might use the sampling pattern previously described, or a composite sampling pattern which offers a representative sample.

Within the Canadian R&D program on environmental aspects of energetic materials, the heterogeneous dispersion of explosives in soil matrices has also been noted when taking samples from biopiles (Ref. 17). Even with extensive homogenization of the treated soil, high spatial heterogeneity variations of explosive concentrations have been observed. Other means of minimizing this heterogeneity problem will be covered in Section 3.1.

### 2.3 Groundwater Sampling

Sampling the groundwater plume of a potentially contaminated site is often the best way to monitor the environmental impact. This is particularly true for explosives, since they are not volatile. CF ranges are often very large areas for which a systematic gridding and soil characterization can results in large expenditures. Thus, a sampling plan involving groundwater can minimize the associated sampling and analytical costs. If contamination is not found in detectable levels in the groundwater on-site also, down and up gradient of the site, it means that the potential contamination does not leach from the site and does not represent a threat to the watertable. If contamination is found in the groundwater, a more detailed sampling plan for the soil must be undertaken, following appropriate sampling procedures recommended in Sections 2.1 and 2.2. All the related work with the installation of wells, pumping and sampling must be conducted with the participation of a hydrogeologist, as described in Chapter 4.

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A detailed protocol for sampling explosive contaminated groundwater was developed as part of a natural attenuation study conducted in the United States by Waterways Experiment Station (WES) scientists (Ref. 18). This protocol suggests to purge the well until stabilization of specific parameters. These parameters include temperature, conductivity, pH, turbidity, redox potential and dissolved oxygen levels. Measurements are taken at each successive half well volume. When three of the parameters are in agreement within approximately 10% of the three consecutive measurements, sufficient water has been purged from the well in order to collect a representative formation sample. The result of these tests should be noted in the sampling logbook. Should these parameters not reach agreement, no more than five well volumes shall be purged. If the equipment needed for monitoring of these parameters is available, the protocol should be followed. In the case where this monitoring would increase the cost or is not available, then we recommend to purge the well of three well volumes before sampling. In most cases, a purging time of thirty minutes is sufficient to achieve this purging volume.

The purging of the wells is necessary since the water within the casing of a well is stagnant, degassed, may react with the screen or casing material and is in an oxidative environment due to the air in contact with the surface of the water. It is therefore necessary to purge a sufficient volume of water from the well to ensure that the sample will be composed only of representative formation water. Purging may be accomplished with either a submersible pump, a low-flow pump or a bailer. The choice of bailer or pump will be based on the depth to the watertable, volume to be purged and permeability of the aquifer. The water retrieved from the well purging should be kept in containers until the analysis reveals the presence or absence of explosive contaminants. Uncontaminated water can be disposed directly on the site, while contaminated groundwater must be treated by passing through an activated charcoal filter before disposal.

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Immediately upon completion of purging, samples should be collected for analysis using either a polytetrafluoroethylene (PTFE)-coated bailer on a PTFE-coated stainless steel cable or the output of the PTFE well tubing when using a Waterra pumping system. A minimum volume of 2 litres of water should be collected in each well and poured into two amber glass containers. Groundwater samples will be collected from the least contaminated wells first to minimize cross-contamination. When a bailer is used for sampling, the bailer should be decontaminated by rinsing three times with acetone and three times with distilled water between each well.

The samples suspected of being contaminated by TNT or TNT derivatives should be stabilized by adding sodium bisulphite (1.5 g/l) since it has been demonstrated that acidification to a pH 2 with this compound is efficient at stabilizing waters containing nitroaromatics (Ref. 19). If samples are to be pre-concentrated using the salting-out solvent extraction (see Sub-section 3.2.1) they must be neutralized prior to extraction or incomplete recovery of the amino compounds will result. If pre-concentration is to be reached using solid-phase extraction (see Sub-section 3.2.2) neutralization is not necessary. Depending on the pre-concentration method used, a sufficient volume of water must be collected in order to obtain the needed number of replicates and to insure quality assurance/quality control by a separate laboratory. The salting-out method requires 770 ml per sample, while the solid-phase extraction requires 500 ml per sample.

The field screening methods described in Section 2.4 can optimize a groundwater characterization campaign by giving real-time information on the levels of explosives found in the collected water phases. Both methods are directly applicable for the on-site analysis of water samples. Field tests may be performed on the pumped stagnant waters to decide on the needed disposal actions. Furthermore, field testing may be a great decision tool in order to determine future well locations by giving on-site information about the contamination. We have successfully used field screening methods for the on-site evaluation in a complete groundwater sampling campaign on the largest OB/OD range

in Canada at Canadian Forces Ammunition Depot, Dundurn (Ref. 20), and it has proven very helpful as a decision tool for the location and number of wells to be installed

#### 2.4 Field Screening Methods

Field analytical chemistry (FAC) is a rapidly growing area of chemical analysis in which the analytical measurement is performed on the site. Traditionally, analysis has been made by collecting a sample from a remote site, transporting the sample to an analytical laboratory, which is often located several days away from the site, and finally storing the sample until the laboratory testing. All this represents an important delay. Days and often weeks are required before the information on the identity and quantities of chemicals in the sample is known. This delay in data availability delays decisions about the sampling site. Some decisions, such as those concerning human safety and product liability, are desired in real time in order to prevent problems. This is particularly true when explosives are the targeted contaminants. We will see in Section 5.1 that the explosive nature can represent a serious threat when manipulating contaminated samples and therefore the need for a reliable field method is essential.

In addition to saving time and promoting safe sampling procedures, FAC can significantly reduce analytical costs. Other real-time decisions such as those concerning environmental remediation or the establishment of a reliable sampling scheme can significantly reduce costs and improve the quality of analytical results. The site can be mapped with respect to analyze concentrations in real time, decreasing the total number of samples required to characterize a site. For explosives such as TNT, RDX and HMX, the cost of field analysis per analyze is lower than laboratory analysis and this approach eliminates the need for transportation and storage. However, a laboratory-based instrumentation provides more precise and accurate analytical data than most field methods. Thus, samples demonstrating a positive response in a field test should then be tested with an approved laboratory method for increased precision. However, the

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colorimetric method described in Section 2.4.1 has been demonstrated to be as accurate and as precise as the High Pressure Liquid Chromatography (HPLC) laboratory method.

Two field methods designed for explosive compounds will be covered in this report. Both methods were tested by DREV and CRREL in many different conditions and the strong and weak points of both methods will be discussed. Furthermore, the most effective use of these methods will be highlighted in order to insure human safety, provide accurate and reliable results and reduce the total analytical costs of future sampling campaigns.

#### 2.4.1 Colorimetric Field Method

The field colorimetric method for TNT, RDX, HMX, ammonium picrate and picric acid has been developed by CRREL US scientists (Refs. 21-26). This method has been developed to detect contaminants that are present on most US military sites. Based on data from sites investigated by CRREL and other DoD R&D laboratories, CRREL determined that most sites could be adequately assessed by employing methods that initially screen for TNT and RDX, and then for secondary 2,4-DNT, TNB, DNB, tetryl, ammonium picrate, picric acid and HMX. They developed a simple, portable method using only low-toxicity solvents which have a quick turnaround time. These methods have a large analytical range, a linear calibration scale and demonstrate sufficiently low detection limits. In addition, CRREL have compared extensively the field colorimetric analytical methods and proved that they correlate very well with standard laboratory methods. These colorimetric methods involve a reaction with the contaminant explosives leading to coloured end products which can be easily monitored with the use of a portable spectrophotometric device. This report briefly describes the colorimetric method developed for TNT, RDX and HMX. The know-how related to these methods has been transferred to industry and the colorimetric test kit is now available at Diagnostix Inc. (Ref. 27). The equipment needed is shown in Fig. 5.

#### 2.4.1.1 Extraction

A simple extraction process is used to first extract the explosives from the soil matrices. A 20 g portion of undried soil from the site is mixed with 100 ml of acetone containing 3% of distilled water. The sample is shaken vigorously for at least 3 minutes, while in some specific cases the kinetics of the extraction process is evaluated to determine if a 3-minute extraction time is sufficient. In some cases, a 30-minute extraction time is recommended to achieve complete extraction of the contaminant (Ref. 14). After the extraction step, the sample is allowed to settle and filtered with a syringe filter. Very heavy clays might need more time to settle, while sandy and loamy soils require as short as 3 minutes to settle. The efficiency of acetone extraction has been compared with the acetonitrile sonication method used in the laboratory and it has proven to be as effective given an extraction time of 30 minutes. The filtered extracts are then subjected to TNT and RDX screening procedures. Furthermore, the same acetone extracts can be used directly when performing the HPLC analysis, as demonstrated in recent trials (Ref. 14).

#### 2.4.1.2 TNT Screening

In the TNT screening procedure, the initial absorbance of the acetone extract at 540 nm is obtained using a portable spectrophotometer. The extract is amended with potassium hydroxide and sodium sulphite, agitated for 3 minutes, and filtered. The extracts can be evaluated visually. If it has a reddish or pinkish colour, it contains TNT; if it has a bluish colour, it contains 2,4-DNT. Figure 6 shows the reaction, known as the Janosky reaction which produces a reddish-coloured anion from TNT and a bluish-coloured anion from 2,4-DNT. The peak at 540 nm is used to verify the presence of TNT, which represents the optimal signal ratio with minimal interferences from humic substances. The field spectrophotometer recommended is the "HACH DR/2010 Portable Spectrophotometer. The results of the TNT screening, which reflect the sum of TNT and TNB concentrations, correlate very well with the results obtained in laboratory.

#### 2.4.1.3 RDX and HMX Screening

Field screening for RDX is similar to field screening for TNT. As in the procedure for TNT, acetone is used to extract contaminants from soil samples. The extract is then passed through an anion exchange resin to remove nitrate and nitrite. This step may be avoided when the site is not suspected of containing detectable levels of these ions. Zinc and acetic acid are added to the extract, thereby converting RDX to nitrous acid. The same reaction will occur with HMX which have a structure and reactivity similar to RDX. Therefore the test can be used for both compounds. The extract is then filtered and placed in a vial with a Hach Nitririver 3 powder pillow. If the extract develops a pinkish colour, it contains RDX or HMX. Figure 7 shows the reaction sequence, including the Griest reaction that produces the pinkish-coloured molecule. As in the TNT detection procedure, quantitative analysis of the extract can be obtained from absorbance measurements. The maximum absorbance of the coloured reaction end-product is at 507, and therefore the reading should be done at that wavelength. The results of the RDX screening, which reflect the sum of RDX and HMX, correlate very well with the results obtained in laboratory.

#### 2.4.1.4 Advantages and Limitations of the Colorimetric Method

The colorimetric field screening method has several advantages. It is quick (30 minutes total per sample), it uses only inexpensive solvents and is very simple to apply with a linear colorimetric analysis demonstrating a zero intercept. The results of colorimetric analysis show strong correlation with those obtained by HPLC procedures. The method demonstrates a low incidence of false negative responses and the detection limits for most analytes are low (Table III).

The main limitation of the colorimetric method is that the procedure is subject to positive interference from humic materials. This might be solved by pre-filtering the

extracts on specific cartridges which will retain impurities. Cartridges used in a new extraction procedure for explosives in groundwater are presented in Sub-section 3.2.1. Compared with the immunoassay field screening method, the colorimetric method requires more in-field manipulations and also requires the use of a field spectrophotometer. However, the colorimetric method produces more precise results, with a larger analytical range (0-200 ppm). Also, recent screening on an anti-tank firing ranges has demonstrated that NC may cause an interference by precipitating in the acetone extract.

#### 2.4.2 Enzyme Immunoassay Field Method

The D-Tech enzyme immunoassay (EIA) method used for both RDX and TNT is commercially available from the same company which provides the colorimetric test kit (Ref. 27). The test kits are named D-Tech Environmental Detection System and were developed in 1994-95 (Refs. 28-29). The components of this EIA include RDX and TNT specific antibodies covalently linked to small latex particles which are collected on the membrane of the cup assembly. A colour-developing solution added to the surface of the cup assembly reveals a colour inversely proportional to the concentration of RDX or TNT equivalent in the sample. RDX and TNT are best measured in the range falling between 0.5 and 5 ppm for TNT and between 0.5 and 6 ppm for RDX. In the case where concentrations higher than 5 ppm are obtained, the dilution of the extracts can be made by a factor of two to four in order to obtain a result comprised within the effective range of the test. All the necessary equipment to apply this field screening method is shown in Fig. 8.

##### 2.4.2.1 Extraction

Soils can either be extracted using D-tech package, or as described above. The ratio of soil/acetone used in the extraction procedures for colorimetric analyses (20 g/100 ml) is considered equivalent to the ratio obtained by using the sampling tube

and the extraction bottles supplied with the D-Tech TNT/RDX soil extraction pack (3 ml sampling tubes/9 ml). Furthermore, the extraction of 20 g of soil instead of 2 g lead to more representative extracts.

#### 2.4.2.2 TNT and RDX Screening

A 1.0 ml aliquot of clear acetone extract is transferred into a bottle of buffer solution (bottle 2 in the extraction pack). The prescribed volumes of soil extracts are added to the vials containing enzyme-labelled RDX or TNT and antibody-coated latex particles. Those mixtures are allowed to stand for 2 minutes (TNT) and 5 minutes (RDX) in order to allow the explosive molecules to interact with the antibodies' binding sites. Negative control references are processed with each analysis. Samples and references receive identical treatment and both solutions are poured into their respective sides (test or reference) of the porous membrane of the cup assembly. The conjugate solutions are allowed to pass through the membranes, washed and treated with a colour developing solution. The reference side of the cup is used to determine the end-point of the colour development. The time for complete colour development is less than 10 and 15 minutes for TNT and RDX, respectively. All of these manipulations and readings are done at room temperature. Unfortunately, the cross reactivity of the RDX test kit towards HMX is low and therefore, this test cannot be applied to screen and HMX-contaminated range.

The results from the test kits are determined with the DTECHTOR environmental field test meter (EM science). This device is a hand-held reflectometer powered with a 9-volt plug-in battery. It measures the amount of light reflected from the surfaces of the colour-developed test and reference sides of the cup assembly. Readings are in percentages which can then be translated into TNT or RDX equivalent concentrations. This procedure is well documented in the field test kit package.

#### 2.4.2.3 Advantages and Limitations of the EIA Field Screening

The requirement for multiple tests per sample, as in the case of high concentrations of explosives increases the manipulations and cost per sample. Also, the D-Tech field screening method can be described only as a semi-quantitative method with inconsistent correlation with the HPLC laboratory method. The use of a reference test and the reflectometer can also represent a limitation since the operator must be very attentive in order to take the reading at the correct time. Erroneous results can easily be obtained should all procedures not be carefully followed. However, this technique has the advantage of being easy to perform in the field and needs minimal space to operate. This is an excellent method to get a quick answer about the order of magnitude of contaminants and can be a good tool to discriminate quickly high and low levels of contamination. The method can be used only as a positive/negative field test to discriminate which samples are to be sent for further laboratory extraction and analysis. Unfortunately, the method is effective only for RDX and TNT. HMX contaminated ranges cannot be screened by the EIA field testing method.

### 2.5 Sample Conservation

The maximum holding time (MHT) for soil and water samples will be described in this section. Detailed information of the MHT is critical to determine the shipping requirements and storing time of the samples in the lab. These factors are important to obtain reliable analytical results from field sampling.

#### 2.5.1 Soil/Sediment Samples

The EPA procedures for explosive-contaminated soils (Ref. 30) specifies a maximum pre-extraction holding (MHT) time of 7 days in the dark at 4° C for both nitramines and nitroaromatics. However, recent reports (Refs. 31,32) have shown that nitramines are stable over an eight week period in identical storage conditions, and that

nitroaromatics were stable for the same period if frozen. Therefore, the MHT can be extended to eight weeks when nitramines are stored at 4°C and nitroaromatics at -20° C. MHT for nitramine-contaminated soil samples can be expanded to six months at -20° C safely, based on their stability at 4° C. Those MHT for soils are reported in Table IV.

### **2.5.2 Water Samples**

Detailed studies on the evaluation of pre-extraction holding times for nitroaromatic and nitramine explosives in water phases were published by CRREL team in 1993, following a comparable study in 1991 (Refs. 33, 34). This study was followed by a subsequent study on the preservation of these water samples (Ref. 19). Both studies included all possible explosives and explosive derivatives that might be encountered in groundwater samples: HMX, RDX, tetryl, TNB, TNT, DNB, 2,6-DNT, 2,4-DNT, 4A-DNT, 2A-DNT, 2-NT, 3-NT, 4-NT and NB.

The first study demonstrated that an acceptable MHT of 50 days can be obtained by using refrigeration at 4° C for both nitramines and nitroaromatics. However, water that might have large microbial activity (such as surface water) might have significant losses of TNB and TNT within a day or two, even under refrigeration.

The second study was oriented towards the establishment of a stabilization procedure to prevent sensitive nitroaromatic loss. In this study, a number of potential options for preservation were considered, including the use of mercuric chloride, sodium azide, chloroform, sodium thiosulphate and acetonitrile with acidification to pH 2 using sodium bisulphate ( $\text{NaHSO}_4$ ). The last choice was selected as the stabilization method to be studied based on the low toxicity of sodium bisulphate and the ease of using a solid stabilizer. The study concluded that MHT for water samples containing nitroaromatics such as TNT, TNB and tetryl can be extended to at least 28 days by acidification to pH 2 using  $\text{NaHSO}_4$ . Acidification did not affect the stability of nitramines that were already stable over a period of 50 days with or without preservation. The data is not available

on the MHT of explosives in water when the samples are frozen, but considering that at -20° C, all microbial activities are stopped and therefore, their MHT can be extended to 6 months safely, as described in Ref. 35. If the solution is frozen it is necessary to ensure that analytes redissolve before analysis. Some explosives such as HMX are slow to dissolve. The MHT for explosives in water samples at both temperatures are reported in Table IV. In conclusion, the MHT reported in Table IV should be carefully followed in any future sampling campaign.

## 2.6 Other Co-Contaminants

When sampling an explosive-contaminated site, parameters other than explosive compounds might be of interest. The activities which might have caused the contamination of soil and groundwater by explosives might also have caused the dispersion of other contaminants in the environment. The most probable one is contamination by metals, since they are either part of the ammunition casing, the ignition system or the target. A screening for metals and heavy metals (as example lead, chromium, aluminium) should be conducted in parallel at ranges where metallic shrapnel is generated and spread on the ground. Mercury should also be investigated where munitions fired at the ranges include this chemical. Also, some activities such as the open burning of obsolete ammunition may lead to the accumulation of polycyclic aromatic compounds in the environment; so these activities should be monitored when the presence of such compounds is suspected.

## 2.7 Air Impact

The impact on the atmosphere of ammunition used in training or destroyed by OB/OD will not be covered in this report. However, the reader interested may consult Refs. 36 to 38 which concentrate on the analysis of gaseous emissions produced by detonation of ammunition. Experiments conducted in a closed vessel (Refs. 36-38) demonstrated that gaseous emissions were almost completely composed of non-toxic

gases. However, an R&D effort is underway at DREV to sample gases in real open detonation situations and to assess the air impact of such activities. Recent investigations and discussions with U.S. scientists tend to indicate that, even if the detonation of ammunition in OD operations does not cause toxic emissions, this may lead to the spreading of heavy metals in the atmosphere and the deposition of these contaminants in areas surrounding the OD ranges. These suppositions are not supported by any sampling data and further research is needed in this area.

### 3.0 EXTRACTION AND ANALYSIS

Because many explosives are often present on contaminated sites, the methods and techniques used in the extraction and analysis of samples must be carefully chosen. Numerous studies for these analytes in water and soil have been addressed in the past to optimize the extraction and analysis to a series of contaminants. (Refs. 39-55). The first part of Chapter 3 will cover optimized extraction techniques that are designed to meet or exceed the requirements of US EPA method 8330 (Ref. 30) and techniques that will allow rapid, precise and a sensitive determination of these analytes in a wide range of matrices. At present, the established extraction technique used for soil extraction is the EPA 8330 sonication extraction. It is a well-proven method used by many laboratories; however, other techniques of soil extraction, such as the accelerated solvent extraction (ASE), may also be used. They are discussed in this chapter. For groundwater extraction, three suitable methods will be discussed; EPA salting out method, the solid-phase cartridge extraction method and the solid-phase microextraction (SPME). Finally, this chapter will cover the optimized analysis methods for the specific series of contaminants. The advantages of both the HPLC 8330 method and the GC-solid-phase microextraction technique will also be discussed in this chapter.

### 3.1 Soil Preparation

A soil preparation method was developed to improve the availability and to minimize the heterogeneity problem of nitroaromatic and nitramine residues in soil. Firstly, soil or sediment samples (~500 g) are visually inspected to ensure that no chunks of solid explosive are present. Soil samples are then air-dried to a constant weight at room temperature. The air-drying process should be done away from sunlight to minimize the photodegradation of TNT and its metabolites. Once the soil is completely dried, the sample is saturated with lab-grade acetone to minimize its heterogeneity and to optimize the availability of the contaminants within the sample. This solubilization step insures a homogeneous dispersion of the explosive contaminant in the soil matrix. Care should be taken to ensure that acetone does not bring the contaminants outside the sample matrix, because an over saturation with acetone could cause contaminants to leach to the edge of the sample recipient. The soil is ground with a mortar and the soil/acetone slurry is thoroughly mixed. The sample with acetone is air-dried again until no traces of acetone are perceptible (24 hours). The soil is then pestled to pass a 25-30 mesh sieve. During all the soil preparation, process care should be taken to avoid cross-contamination between the samples during the different manipulations. Finally, the soil sample is covered with aluminium foil and conserved for extraction.

### 3.2 Soil Extraction

The EPA 8330 sonication in acetonitrile is the mostly used technique to extract explosives from the soil matrices. Other techniques might also be used such as the accelerated solvent extraction, solid phase microextraction (SPME) or even a simple extraction with acetone. This chapter provides additional details on the sonication, ASE, and acetone extraction techniques, describes the advantages and disadvantages of each one, and indicates different experimental parameters that may be used for better recovery.

### 3.2.1 EPA Sonication in Acetonitrile

Extraction by sonication is described in Ref. 30. A 4.0-g subsample of a homogeneous dried soil sample is placed in a 25 X 200 mm test tube equipped with a teflon-lined screw cap. A 20-ml aliquot of acetonitrile is added, and the soil is shaken by vortex mixing for 1 minute. The use of a vortex mixing apparatus is recommended because manual shaking styles are likely to be different among laboratories (Ref. 45). The soil sample is then placed in an ultrasonic bath for 18 hours. The bath is maintained at ambient temperature during extraction to minimize thermal degradation (Ref. 45). The vials are removed from the bath and allowed to settle for 30 minutes. A 5-ml aliquot is removed, placed in a glass scintillation vial and combined with 5.0 ml of aqueous  $\text{CaCl}_2$  (4g/L). The vials are shaken and allowed to stand for 15 min to allow the fine particles to flocculate. A 5-ml aliquot is filtered through a 0.45 mm Millex filter into a clean scintillation vial. Extracts are stored at 4°C in the dark, wrapped in aluminium foil, until analyzed. The main advantage of this technique is that it has proven to be particularly suitable for explosive analytes in soils. Another advantage with sonic bath extraction is the opportunity to extract contaminants from soils without using temperature variations. The extraction is performed using ambient temperature, which eliminates most of the risks of thermal degradation of some compound. In addition, a large number of samples can be processed simultaneously in a ultrasonic bath. Finally, the main disadvantage of sonication technique is the long process time (18 hours); however, with good planning, it should not be considered as a critical disadvantage.

### 3.2.2 Accelerated Solvent Extraction

In the last few years, various attempts have been made to replace the classical extraction techniques. In this section, we will discuss a new technique, called accelerated solvent extraction ASE, brought by Dionex inc. The accelerated solvent extraction technique can be faster, less time-consuming, and uses less solvent than conventional soxhlet extraction or sonication extraction techniques (Ref. 56). The technique makes use

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of solvents, such as acetonitrile, acetone, methanol or a mix of them, which are pumped into an extraction cell (11 - 33 g) containing the sample. The extraction cell with the sample is then brought to an high temperature and pressure to reduce the extraction time. Minutes later (15-25 min) the extract is transferred automatically from the heated cell to a standard collection tube ready for filtering and analysis. ASE method is a quick process capable of extracting one sample in 15-25 minutes compared with 18 hours for sonication. It also has the advantage of requiring minimum solvent (less than 15 mL for a 10-g sample). A recent study was published by Dionex on the extraction of explosives from soil using this technique (Ref. 57). The results indicate that the ASE method is equivalent or superior to sonication method for the extraction of explosives and their metabolites in soils (Ref. 57). Table V summarizes the percentage recovery of TNT, RDX, HMX and DNT using the ACE technique. Using ASE, complete sample extraction can be done without operator intervention once the instrument is loaded and started. Even though this technique of extraction has many positive qualities, care should be taken since it is relatively new and requires further testing. The Dionex ASE 200 can perform 24 cell extractions in one run which brings the extraction time for 24 samples up to 6 to 10 hours compared with 18 hours for the sonication technique. Also, ASE operates at high a temperature (100°C) meaning that thermal degradation could be a potential concern. Furthermore, when working with highly contaminated samples, heating to 100°C may represent a risk.

The operating conditions of the Dionex ASE 200 accelerated solvent extractor are as follows: System Pressure: 1500 psi, oven temperature: 100°C, sample size: 2.5 g to 30 g, oven heat-up time 5 minutes, static time 5 minutes, flush volume 60%, solvent acetone or methanol, purge 1 MPa (150 psi) nitrogen for 200 seconds, one static cycle, extraction time 14 minutes and solvent volume 17 to 50 ml per sample.

### 3.2.3 Acetone Extraction

Another possible extraction method is the direct extraction by shaking the sample in acetone. 20 g of dried soil is placed in an extraction bottle filled with 100 ml of acetone and shaken vigorously for 30 minutes by vortex. This extraction procedure was recently compared with the EPA sonication (Ref. 14-15) and proved to be equally effective at extracting explosive compounds. Acetone extracts can also be injected directly for HPLC/UV analysis after dilution with water (1:5). The limitation is the fact that acetone absorbs in the UV, then the separation used, needs to take this into account. LC-CN columns can be used for acetone extracts but it is not appropriate for all applications.

## 3.3 Groundwater Extraction

The aqueous samples require an initial preconcentration step before analysis to enable measurements in the low parts-per-billions ( $\mu\text{g/L}$ ) range. This preconcentration step can be performed by using a salting-out method, a solid-phase extraction (SPE) method or with solid-phase microextraction (SPME) followed by GC analysis. In the past, EPA salting out method has been the predominant method of choice to preconcentrate contaminants. Today, many laboratories are also employing the SPE technique due to many advantages brought with this technique.

### 3.3.1 EPA Salting Out Method

The EPA salting out preconcentration procedure is well detailed in Ref. 30. Briefly, a 251.3-g portion of reagent-grade sodium chloride is added to a 1-L volumetric flask. A 770-mL sample of water is measured with a 1-L graduated cylinder and added to the flask. A stir bar is added and the contents are stirred at maximum RPM until the salt is completely dissolved. A 164-mL aliquot of acetonitrile (ACN), measured with a 250-mL graduated cylinder, is added while the solution is being stirred, and stirring is

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maintained for at least 15 minutes. If the ACN is slow in dissolving due to poor mixing, a Pasteur pipette is used to withdraw a portion of the undissolved ACN (i.e. appears as a separate phase) for reinjection into the vortex of the stirring aqueous phase. After equilibrium has been established, only about 5 mL of ACN should remain in a separate phase. The stirrer is turned off and the phases are allowed to separate for 15 min. If no emulsion is present, the ACN phase is removed and placed in a 100-mL volumetric flask and 10 mL of fresh ACN is added to the 1-L flask. The 1-L flask is again stirred for 15 min, followed by a 15 min setting phase for separation. The ACN is removed and combined with the initial extract in the 100-mL volumetric flask. When emulsions are present, that portion of the sample is removed from the volumetric flask with a Pasteur pipette, placed in a 20-mL scintillation vial and centrifuged for 5 min at 2000 rpm. The supernate is also pipetted into the 100-mL volumetric flask, the scintillation vial is rinsed with 5 mL of acetonitrile, and the acetonitrile is added to the 100-mL volumetric flask.

To reduce the volume of ACN, an 84-mL aliquot of salt water (325 g NaCl per 1000 mL of water) is then added to the 100-mL volumetric flask. The flask is placed on a vertical turntable and rotated at about 60 rpm for 15 min. After allowing the phases to separate for 15 min, the ACN phase is carefully removed using a Pasteur pipette and placed in a 10-mL graduated cylinder. An additional 1.0-mL aliquot of ACN is then added to the 100-mL volumetric flask, and the flask is rotated on the turntable for 15 min. Again the phases are allowed to separate for 15 min, and the resulting ACN phase is added to the 10-mL graduated cylinder. The volume of the resulting extract is measured and diluted 1:1 with reagent-grade water prior to analysis (Refs. 30, 45). The salting out method for preconcentration has been extensively studied and is the EPA accepted method. However, this method is time and solvent consuming, requires very careful steps and may often be jeopardized by emulsion problem. The detection limits offered by this method are also relatively high especially when analyzing drinking water where threshold limits are very low.

### 3.3.2 Solid Phase Cartridge Extraction

Solid-phase cartridge extraction has been recently studied as an alternative pre-concentration method for explosives in water (Ref. 58). Briefly, prepacked cartridges of Porapak RDX Sep-Pak, 6 cc, 500 mg (Waters Corporation) are cleaned by placing them on a Visiprep solid-phase extraction manifold (Supelco) and passing 15 mL of acetonitrile through each cartridge at gravity flow. The acetonitrile is then flushed from the cartridges using 30 mL of reagent-grade water. Care is taken to insure that the cartridges are never allowed to dry after the initial cleaning.

A connector is placed on the top of each cartridge and fitted with a length of 1/8-in.-diameter Teflon tubing. The other end of the tubing is placed in a 1-L flask containing 500 mL of the sample. The vacuum is turned on and the flow rate through each cartridge is set at 10 mL/min. If the flow rate declines significantly due to partial plugging from suspended material, it is readjusted. After the sample is extracted, the top plug containing the fitted tubing is removed from each cartridge, and 10 mL of reagent-grade water is passed through the cartridge using gravity flow, unless the cartridges are sufficiently plugged to require vacuum. A 5-mL aliquot of acetonitrile is used to elute retained analytes from the cartridges under gravity flow. The volume of recovered ACN is measured and diluted 1:1 with reagent-grade water prior to analysis.

Solid-phase cartridge extraction (SPE) has several advantages, including the speed at which a sample can be concentrated and extracted. It is a technique that brings excellent recoveries and reproducibility and it also requires less solvent than the salting-out method. Also, it is inexpensive and easy to use. However, SPE cartridge extraction also has several disadvantages. There is a necessity to use a clean solid phase, because interferences might be released from certain water matrices. Also, it is difficult sometimes to pass all the water sample through the Sep-Pak cartridge, due to the solid sediment occasionally present in certain water samples. However, when comparing the advantages and disadvantages of the two methods of extraction, it is strongly recommend

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that the SPE method be used. Recently, the SPE alternative has been given preliminary approval for use by the US EPA Office of Solid Waste and is being issued as Method 3535 (A).

3.3.3 Solid-Phase Microextraction Followed by GC Analysis.

Solid-phase microextraction (SPME) is a solventless rapid extraction technique that uses polymer-coated fibres to remove organic compounds from an aqueous or solid-phase sample followed by thermal desorption in the injection port of a gas chromatograph for subsequent detection and quantification. The technique is known for its speed and sensitivity, which enables detection in the  $\mu\text{g/L}$  range (Refs. 59-65). Apart from being environmentally friendly and cost-effective, this solventless sample preparation technique, SPME, allows for the detection of pollutants at trace levels, thus providing the information needed to monitor the fate of explosives at the site.

In the present study we will mainly address the use of this rapidly evolving technique as a potential tool to characterize explosives in soil/water systems. Studies will also verify the ability of the technique to analyze TNT intermediates which are produced by solar radiation and/or by aerobic and anaerobic biodegradation using the soil microbial flora. These reactions are considered important in determining the fate of explosives in the natural environment, e.g. natural attenuation.

In the SPME technique, a fine fused silicon fibre with a polymeric coating is used to extract the explosives and their metabolites from their matrix. Then it is directly transfer to the injector of a gas chromatograph (GC) for chemical desorption and analysis by a suitable detector such as MS. In a typical SPME-GC/MS analytical setup, a Supelco Polyacrylate fibre autosampler assembly (85-mm film thickness) is used to collect (adsorb) and inject (desorb) the analytes either from a soil or water matrix. The SPME/GC-MS technique was validated by preparing known concentrations of TNT in aqueous solutions. The concentrations were then determined by both SPME/GC-MS and

by the HPLC-based EPA Method # 8330. In performing the analysis, a stock solution of TNT in acetonitrile was prepared (1000 mg/L) and specific volumes were taken and diluted with different volumes of deionized water. These samples were then subsequently analyzed in triplicates by both SPME/GC-MS and HPLC/UV ( $\lambda$ 254nm). Figure 9 shows that concentrations of TNT found by both techniques are comparable especially at low concentrations. This is in agreement with the linear range of the SPME response, which favours low concentrations. This data supports the potential use of the solventless SPME as a field monitoring tool for site characterization, particularly at low concentrations. Unfortunately, this technique does not apply to more sensitive nitramines.

### 3.4 Extracts Analysis

Many explosives are thermally labile and hydrophilic and consequently should not be analyzed using certain tests and solvents. For example, gas chromatography (GC) in particular, is not the best choice to screen for these compounds, because they decompose. Alternatively, HPLC has routinely been selected laboratory analysis of soils and groundwater containing explosives (Ref. 30). However, the GC analysis method like SPME-GC can be used for some tasks, as described in Sub-section 3.4.2.

#### 3.4.1 Soil/Groundwater Analysis by HPLC EPA 8330

The reversed-phase high-performance liquid chromatographic (RP-HPLC) procedure, issued by the EPA Office of solid waste as SW846 Method 8330, has been accepted by DREV and other laboratories for the analysis of nitroaromatic and nitramine explosives in soil. This method is based on solvent extraction of analytes from soil using sonication and salting out extraction for groundwater. Followed by an isocratic-HPLC separation and UV detection. Detection limits for 15 individual compounds (HMX, RDX, TNB, DNB, tetryl, NB, TNT, 2-ADNT, 4-ADNT, 2,6-DNT, 2,4-DNT, 3,5-dinitroaniline, and the three isomers of NT) are all less than 1  $\mu$ g/g (table VI). Also, all analytical explosive standards for method EPA 8330 are available from AccuStandard® for (international orders, call 203-786-5290).

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Two HPLC instrument conditions have been used at DREV for the analysis of nitroaromatic and nitramine explosives in soil and in groundwater. The first version is used for the rapid analysis of HMX, RDX and TNT. This version has the advantages of offering good separation of the three analytes and it decreases greatly the analysis time for each sample (10 minutes for each sample). The calibration curve is generally composed of three points 0.5, 5, 25 ppm. The main setup conditions are: Column: A supelco LC-18 reverse phase HPLC column (25-cm X 4.6-mm, 5 $\mu$ m) or equivalent, mobile phase: 50/50 (v/v) methanol/organic-free reagent water, flow rate: 1.5 mL/min, injection volume: 100- $\mu$ L, temperature 30°C, UV detector: 254-nm.

The HPLC can also be used for the analysis of 15 analytes (HMX, RDX, TNB, DNB, tetryl, NB, TNT, 2-ADNT, 4-ADNT, 2,6-DNT, 2,4-DNT, 3,5-dinitroaniline, and the three isomers of NT.). This long version (45 minutes) offers effective separation between all analytes. The calibration curve is also generally composed of three points with analyte concentration of 0.5, 5, 25 ppm. The main set-up conditions are: Column: Waters Nova-pak C-8 (3.9X150 mm) or equivalent, mobile phase: 82:18 water/Isopropanol, flow rate: 1.0 mL/min, injection volume: 100- $\mu$ L, temperature: 24°C, UV detector: 254-nm.

A UV wavelength of 254 nm is used for detection in the two methods, because all analytes of interest absorb strongly at this wavelength. Results are generally obtained in the peak height mode, which is found to give better reproducibility for low-concentration samples. Chromatographic analysis uses a system with photodiode array detection. It is a rapid and simple peak confirmation with a high sensitivity, that compares and confirms compound identity with a standard library (Ref. 48).

### 3.4.2 Solid-Phase Micro-Extraction GC/MS

The use of this particular technique might be of interest when analyzing samples suspected of being contaminated with ppb levels of TNT or TNT by-products. The

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separation by GC and analysis by MS allows ppb level detection of these specific chemicals. We have carried out the separation of these chemicals with a Varian 3400 GC connected to a Varian Saturn II ion trap. An absorption time of 20 minutes at room temperature and a desorption time of 10 minutes at 260°C in the injection port of the GC are found to be suitable to optimize quantitative results. The SPME/GC-MS chromatogram shown in Fig. 10 is an example of TNT biotransformation, namely 2-ADNT, 4-ADNT, 2,4-DANT and 2,6-DANT. These metabolites were identified by their spectra (m/z) and base peak (bp) and by comparison with internal standards. The m/z (amu) and bp (amu) for the four detected intermediates were 2-ADNT (197, 180), 4-ADNT (197, 180), 2,4-DANT (167, 167) and 2,6-DANT (167, 167). This detection technique was tested and found suitable for TNT and TNT derivatives but offers a high sensitivity when low concentrations are to be analyzed. Also, SPME can be interfaced with HPLC for other explosives analysis. In conclusion, SPME/GC-MS is a versatile technique that may be successfully used to analyze explosives on contaminated sites, particularly in the groundwater. It can also be used to monitor the fate of explosives in an open environment where the compounds are exposed to solar radiation, aerobic and anaerobic microbial flora. SPME/GC-MS can thus be a beneficial monitoring tool to assess the changes that explosives may encounter on a site, including transportation, transformation mechanisms, and interactions between the explosive and other soil components.

Recently, a GC-ECD method, which is applicable to both TNT, RDX and HMX, has been developed by CRREL. This technique might be of interest when analyzing samples suspected of being contaminated with ppb levels of these contaminants in water matrices (Ref. 66).

4.0 ENVIRONMENTAL FATE OF EXPLOSIVES4.1 Relative Fate of Explosives

Explosives such as TNT, RDX and HMX are crystalline compounds. One can see in Table I that these compounds have low vapour pressure and low water solubility. Their crystalline properties result in heterogeneous dispersion in the soil matrix which makes them difficult to characterize. The sampling procedures were modified to take this behaviour into account, as described earlier in Section 2.1. Explosives behave differently from each other, depending on the water solubility and structure. TNT is more soluble in water than RDX which in turn is more soluble than HMX. Also, TNT dissolve more rapidly compared with RDX and HMX (which dissolves slower) in some initial experiments. TNT is a nitroaromatic, while RDX and HMX are nitramines. TNT has a great tendency to degrade by photolysis, while RDX and HMX do not. In addition to their differences in solubility, TNT itself can degrade into 21 metabolites which possess their own solubilities and toxicities. As an example, the aminodinitrotoluenes resulting from the photolysis or biodegradation of TNT are much more soluble than the parent compound, but can covalently bound to humic acid. Therefore, these metabolites are stabilized by the formation of an amide with organic contents of the soil. Moreover, sorption mechanisms with soils containing clays are stronger with TNT and its metabolites than for RDX and HMX, which adsorb very poorly to clays minerals and some others (Refs. 67-70).

Therefore, a soil multicontaminated by these three explosives would make the situation more complex and as a result, RDX will leach out faster than TNT which will leach out faster than HMX. RDX, being more soluble than HMX and less soluble than TNT, moves faster because it does not adsorb on soils. TNT being the most soluble of the three compounds should leach first but, as already mentioned, it adsorbs strongly to clay minerals or degrades into metabolites which, even when more soluble than TNT, binds covalently to the clays. This process of adsorption/desorption slows down the speed

of migration of TNT into soils. HMX being almost insoluble in water has a great tendency to stay on the surface of the soils. For example, a site contaminated by octol (HMX/TNT 70:30) shows a cumulated high concentration of HMX at the surface, but TNT is not detected or at least is not present in the right proportion. Based on their physical and chemical properties, one could hypothesize the following: TNT which was originally present in the mixture at 30% was solubilized by rain and migrated through soil leading to a lower concentration on the surface. Another possibility is that photolysis or biodegradation of TNT resulted in the formation of more soluble metabolites which migrated into the soils and bind to organic matter. These metabolites, being covalently bound, could not be extracted and analyzed by EPA 8330 HPLC method. On the other hand, HMX being much less soluble (much slower also) in water (4 ppm) stays at the surface where it is detected and, moreover, the concentration increases if the site becomes contaminated with additional HMX.

Interactions with the soil are therefore important aspects to consider when characterizing explosives in terms of bioavailability and extractability. One explosive that is particularly difficult to characterize is TNT as it is easily reduced to form amine degradation products, namely 2- & 4-aminodinitrotoluene (ADNT), 2,4- & 2,6-diaminodinitrotoluene (DANT), and, under anaerobic conditions, 2,4,6-triaminotoluene (TAT). The characterization of TNT derivatives is important since they play a major role in establishing the overall toxicity, remediation, transport, and extractability of TNT. The adsorption and desorption characteristics of TNT and its metabolites are important physical factors to consider when assessing the availability of the compounds to microbial degradation and physical analysis.

Organic contaminants can be adsorbed onto the soil particles via hydrophobic,  $\pi$ - $\pi$ , and Van der Waals interactions or undergo chemisorption by reacting with humic and fulvic acids. Strongly adsorbed contaminants will be more difficult to remediate and analyze than the weakly adsorbed ones. This is especially true in the case of TNT, whose metabolites have been found, in this study, to bind much strongly than TNT itself to the

soil (Figs. 11 and 12). Soil/water mixtures were shaken for 16 h (1 h for TAT) and centrifuged. The analyte concentration in the aqueous phase was determined by HPLC (EPA method 8330) and the concentration in soil was determined by the difference. A non-linear form of Freundlich equation,  $Q=K_d C^N$  was used to describe the absorption of TNT, where  $Q$  is TNT adsorbed per gram of soil,  $K_d$  is the distribution coefficient of the contaminant between the soil and liquid phases,  $C$  is the equilibrium concentration of TNT in the liquid phase, and  $N$  is a constant (Fig. 11). For the desorption study, fresh distilled water containing no analyte was added to the same soil used in the adsorption study. The reduction of the nitro groups had a notable effect on adsorption, the degree of which was dependent on the number of substitutions. Figure 11 clearly demonstrates the effect of monosubstitution of TNT on adsorption. A steep adsorption curve means strong adsorption and it can be seen that there is a significant increase in adsorption upon monosubstitution, with the distribution constant ( $K_d$ ) increasing from 1.3 to 17.6 for 2-ADNT. The reduction of a second nitro group to form 2,4-DANT raised the  $K_d$  value even further to 42.1.

Adsorption studies were performed with 2,4,6-triaminotoluene, a derivative believed to be formed only under anaerobic conditions (Ref. 63). However, no TAT was detected in the liquid phase during the batch studies, indicating that there was either complete irreversible binding to the soil matrix and/or TAT underwent polymerization. Subsequent extractions with methanol did not recover TAT from the soil.

The desorption curves (Fig. 12) in water showed the same trend as the adsorption curves. The partition coefficients increased with increasing amino substitution on the ring. As was the case with adsorption, the desorption of triaminotoluene in water showed complete irreversible binding to the soil. The final fate of TAT, whether bound to humic substances or polymerized, is not known at this point. It appears, though, that the formation of TAT can lead to a loss of bioavailability during a soil remediation process if it binds irreversibly to soil particles.

It is important to note that adsorption and desorption is a function of soil type and that the severity of adsorption will depend on parameters such as clay content, organic matter composition, and humidity. Adsorption and desorption of the explosives would have to be determined in each soil that is being characterized. Soil sorption isotherms, which are structured and controlled according to the nature and extent of soil/contaminant interactions, dictate the contaminant bioavailability to degrading microorganisms, toxicity assays, extractions and migration. In conclusion, the relative fate of the various explosives and metabolites should be considered when characterizing a site in order to obtain the best possible analytical results from contaminated samples. More R&D is needed towards the development of an optimal extraction method for TNT metabolites which are strongly bound to clay or organic soils.

#### 4.2 Subsurface Sampling

As already mentioned, the explosives can be slowly solubilized and migrate towards the groundwater leading to the formation of a plume. In order to understand the size and the direction of the contaminant plume and also to evaluate the impact on the environment, well drilling and installation are essential to sample the groundwater. The services of a drilling firm specialized in contaminated site assessment is required to install nested wells with 2-4 m depth levels to establish the contaminant profile. Boreholes drilled have to be equipped with observation wells with a 5-foot screen. The maximal depth of drilling is related to the depth of the groundwater at the specific site.

##### 4.2.1 Boreholes Drilling and Soil Sampling

The local stratigraphy of the site is determined by examining existing boreholes logs usually available from the Department of Environment. The thickness of unconsolidated material can then be assessed. The proposed boreholes and monitoring wells are located taking into account the geology and the topography of the site. Hydrogeologists should be involved at this step to evaluate the direction of groundwater

flow and the likely extent of the contaminant plume. The drilling depth of the boreholes is defined on-site, depending on the observations made from the first drilling.

The vibrasonic method or hollow stem auger with split spoon should be used for sampling. Preferably, boreholes will have to be drilled without using drilling fluid. If the vibrasonic method is selected for sampling, any ODEX type drilling method can be used for drilling boreholes designed for observation wells installation. For each borehole, a well log should identify all geologic formation present in the unconsolidated material. Initial borehole diameter in unconsolidated material should be sufficiently large to allow the installation of 2-inch monitoring wells.

Soil samples are collected at different depths by split spoon. A good procedure consists in sampling at each 5 feet and analyzing the soils by Dtech test kits or EnSys colorimetric test kits. If contaminated, further analysis by US EPA 8330 HPLC method should be done. By doing so, a three-dimensional map may be constructed and a better understanding of the contamination is obtained. Washing of the split spoon is accomplished by immersing it in a hot water barrel and cleaning or by removing the dirt with high pressure steamed water. Acetone is then spayed on the split spoon to remove the last traces of explosives followed by spraying distilled water.

#### 4.2.2 Monitoring Well Installation

Each borehole should be equipped with a monitoring well installation. The well depth will be defined on the field, depending on the information obtained from the first drilling. The well's components (well casing, joints, screen, filtering pack, expansive cement, cement/bentonite mix or bentonite silt, protecting casing...), their dimensions, and installation must be in accordance with the requirements presented in the document «Guide d'échantillonnage à des fins d'analyses environnementales», cahier *Échantillonnage des eaux souterraines* (ISBN 2-89443-006-X), published by Le Griffon d'argile, or prescribed by the ASTM-D5092-90 norm. The well's installation is also described in the

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Natural Attenuation Protocol published by WES scientists (Ref. 18). No other seal material than those required by the guideline or by the standards should be used in the space between the permanent well casing and the borehole wall. The well's permanent casing and screen should be made of PVC. Five-foot well screens should be used. Each well elevation must be established from the top of the PVC permanent casing. A report describing boreholes locations, depth of drilling, local geological stratigraphy (drilling log), identification of the drilling method used and the specifications related to the well's installation is then written.

A protective casing with locks should be installed on each well. This is intended to protect the piezometers from outside contamination and also from mechanical shock which could permanently damage the piezometer. Usually, the well casings are installed over the top and they are 2 feet high. When installing a well casing over piezometers, which are located in the range that could be subject to impact by explosions, it is recommended that the protective well casings be surface mounted. These well casings should be installed in concrete to provide the needed protection.

5.0 SAFETY PROCEDURES

Secondary explosives or also referred to as high explosives like RDX, HMX and TNT have specific chemical, physical and toxicological properties. The explosive characteristics of these environmental contaminants represent a major difference compared with conventional contaminants. Therefore, the explosive characteristics must be carefully integrated in the hazard analysis and safety protocol. Secondary explosives can lead to reactions of either detonation, deflagration, burning or high rate decomposition under various stimuli, such as heat, shock, friction and electrostatic charge. Thus, specific safety procedures have been developed for sampling at explosive-contaminated site. Their toxicological characteristics also have to be considered to ensure proper safety of the sampling team. A final consideration, in many sites belonging to DND, is the presence of unexploded ordnance that might be found on the site. This represents a unique and

important risk which must be understood and properly managed. All these aspects will be covered in this chapter.

### 5.1 Explosive Nature of Contaminants

Safety precautions must be taken at the sites contaminated with explosive waste. The United States has been involved in sampling and treating explosive waste for many years. They have developed safety protocols and handling procedures for the potentially contaminated sites. They have developed a sensitivity testing protocol for determining whether soils contaminated with explosive waste are likely to initiate and propagate, and, if so, how to best handle them. This original protocol involves many tests, including impact tests, friction and shock gap tests and the deflagration-to-detonation test, which measures the explosive's reaction to shock. The drawback of this protocol is that these tests require relatively large volumes of soil to be excavated and shipped to specially qualified laboratories, often at great expense.

The experience gained by conducting sensitivity tests on many contaminated sites containing different levels of contamination revealed that explosive contaminated soils might be treated as normal soils. However, they also determined that soils containing more than 12% secondary explosive by weight are likely to initiate and propagate. As a conservative limit, it is considered that a soil containing more than 10% secondary explosives by weight (100,000 mg/kg) must be considered as explosive and a number of safety precautions must be implemented when sampling and treating these soils.

It should be noted that concentrations as high as 100,000 ppm of secondary explosives are rarely encountered and often a visual inspection will identify the presence of pieces of pure explosives in the soil. From our experience in sampling many DND sites, these high levels are not to be expected in any ranges since CF activities do not lead to high levels of explosive contamination. These high levels might, however, be found in old explosive production sites, where production waste has been dumped directly on

the soil or in lagoons. The slow evaporation of these lagoons might have allowed the accumulation of high levels of explosives in the sediment.

The first step when planning a sampling campaign on an explosive-contaminated site, is to review all the historical information available at the site and to perform a visual inspection of the range. When a site is suspected of being contaminated with high levels of explosives, a preliminary sampling of the worst contaminated area should be carried out. Only surface soil samples should be taken and no drilling should take place. Cautious subsurface sampling or shovelling might be performed, using non-sparkling hand augers at shallow depth. Representative composite samples of the worst area should be built and analyzed. This is a good example of where the field methods described in Section 2.2 may be applied. Since these tests can be performed in the field, immediate results are obtained to assess the potential risks. Both field EIA and colorimetric methods can be used for this purpose, by diluting the acetone extracts in order to reach the effective analytical range of the methods. However, the colorimetric method should be employed first, since it is easier to assess the initial concentration. High levels of contamination will lead to intensively coloured extracts that will give an approximation of the dilution factor that will have to be applied to reach the analytical range. A specific protocol for use of the colorimetric methods for high level samples has been developed (Ref. 71). On the other hand, the EIA method will lead only to a "high" response for sample contaminated with more than 5 or 6 ppm of explosive. Furthermore, the EIA method will not react significantly with samples contaminated with HMX thus, high levels of this explosive will not be detected.

In the case where levels higher than 10% by weight are encountered, safety precautions will have to be implemented. The most important safety precaution is to minimize exposure, which involves reducing the number of workers exposed to the hazardous situation and limitating the duration of exposure on site. To reduce the hazard at explosives wastes sites, physical activities should be carried out on materials that have been diluted to a wet slurry. If needed, water should be added to the soil to achieve the

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desired moisture content. Water desensitizes the explosive by flegmatizing it and it also reduces the effect of heat and friction. The drawback of adding water is the possibility of leaching more explosives to the groundwater. However, this is a minimal environmental impact compared with the leaching created by rainfall and it will insure the safety of the personnel who will have to manipulate these soils. Another safety precaution is the use of non-sparking tools, conductive and grounded plastics and no screw tops, which have been developed for manufacturing explosives. For example, non-sparking beryllium tools might be used instead of ferrous tools.

If an operation involving mechanical shovelling is needed, remotely controlled operations would offer the best protection. When this is not possible, armoured safety glasses must be installed in the operator compartment. Drilling operations should only be permitted after removing the soil layer that is contaminated above the safety level. Drilling operations may then be performed on the remaining soils. Equipment used in treatment must have sealed bearings and shielded electrical junction boxes. The equipment must also be decontaminated frequently to prevent the build-up of explosive dust.

If contamination is above the 10% limit in the soil samples, the contaminated material should be blended and screened to dilute the contamination and produce an homogeneous mixture below the limit. This dilution is not a remedial action by itself but a safety measure that will allow the safe handling, storing and shipping of samples. The blending should be done precisely in order to calculate the initial concentration that was present in the sample. If the soil were not diluted, the transport of the samples would require the same safety waiver as that required for transporting pure secondary explosive material.

## 5.2 Toxicity Associated with Explosives

In addition to the explosivity associated with energetic compounds, some toxicological aspects must be taken into consideration. Secondary explosives are considered carcinogenic and mutagenic. The toxicity of explosive chemicals has been studied extensively by the U.S. Army Biomedical Research and Development Laboratory and a summary of these investigations has been published (Refs. 72, 73). As an example of their human health related toxicities, Table VII presents the drinking water criteria for six explosive compounds (Ref. 9) for a lifetime exposure cancer risk level of  $10^6$ . The low acceptable threshold criteria for these compounds in drinking water indicate their high levels of toxicity.

No general recommendations have been issued for explosive contaminant levels in soils. In the United States, the threshold levels in soils are evaluated on a site-by-site basis, depending on factors such as the proximity of the contaminated soils to other locations and the use of surrounding groundwater. For example, on an ammunition plant, cleanup criteria of 5 ppm for TNT, 10 ppm for RDX and 15 ppm for HMX were established for the protection of the groundwater. These threshold criteria take into account the fact that the site will not be used in the future for any residential or recreational activity.

On the other hand generic criteria for soils and groundwater were calculated by Daniels and Knezowitch in 1994 (Ref. 74). The same human health-based criteria were calculated by using a Canadian model under a DREV contract in 1997 (Ref. 75). The human health criteria for soils calculated by both team are reported in Table VIII.

The latest threshold criteria are very severe and do take into account all possible intakes of these compounds by humans. Many exposure pathways considered in the calculation of the criteria are not encountered in real-site situations and therefore, the levels recommended are probably too severe. The evaluation of site-by-site threshold

criteria as it is performed in the U.S. appears to be the best choice to obtain threshold criteria that are realistic and will still protect human health. This can be achieved by a detailed site risk assessment which considers all possible exposure pathways relative to the site.

In Canada, no generic threshold criteria have been published for explosives. However, an important effort is conducted presently to establish Canadian ecotoxicological-based threshold criteria. A site risk assessment approach will probably be the best choice for addressing this problem in the future. However, it is still important to take the toxicity of these explosives into account when sampling an explosive-contaminated site.

Explosive compounds are not volatile, with the exception of NG. Therefore, no specific precautions must be taken to prevent the inhalation of explosive vapour. If NG is a possible contaminant, a strong organic odour will be detected on the site. If this is encountered, an organic vapour protective respiratory mask should be worn at all times during the sampling and manipulation of these soils or water samples. For the other energetic compounds, this protective equipment is not needed. However, explosive crystals dispersed in the soil might be carried away with soil dust, and a dust mask must be worn by the sampling team when dry sandy or clay type soils are encountered.

Protective clothing, gloves and glasses should be worn in all situations to avoid possible dermal contacts with the contaminated media. Those recommendations should be followed in all field screening and laboratory manipulations of samples involving pure explosives or stock solutions.

### 5.3 Unexploded Ordnance Clearance

Many CF potentially contaminated sites, such as firing ranges, present a high probability of contamination by unexploded ordnance in addition to soil contamination by

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pure compounds. Unexploded ordnance could be the main source of contamination at the range, since ammunition duds are often fractured or broken leaching contaminants in the environment. These dispersed duds represent a high risk level when carrying out site investigation or remediation projects on the site. These duds are unpredictable and may be highly unstable since they are often exposed to environmental variations for long periods. Dud-fired munitions are often still fuzed and armed.

Specially trained military personnel such as ammunition specialist, field engineer or specialist contractors have the expertise to take care of this situation. They can perform clearance of the contaminated site at three different levels of safety: Level one clearance: consisting in identifying only surface duds by visual observation of the site. Level two clearance: Consisting in clearing a layer of soil of 30-45 cm depth from duds with the help of a magnetic detector. Level three clearance: Consisting in cleaning completely the area of the site to any depth until nothing is detected.

Ideally, a level-3 clearance of a contaminated area should be performed before a soil characterization program or remedial action plan is undertaken. This high-level clearance ensure the greatest safety and also allows the drilling of wells directly on the site. However, this operation might be economically or physically unfeasible and level-1 or 2 clearance may still provide a safe working environment. In addition, level-3 clearance disturbs the soil profile and it is impossible afterwards to characterize depth distribution of explosives. No drilling operations should be conducted until a level-3 clearance has been performed. Remote control drilling could be another option to level three clearance.

Cautious surface sampling can still be achieved after level-1 or 2 clearance operations, but an ammunition specialist or a field engineer must be present at all times during the sampling operation in order to ensure that proper procedures are followed. When shovelling or implanting grids on the site, the verification by a specialist of the

absence of metallic debris underneath the surface soil must be made with the help of a portable metal detector.

In conclusion, the characterization of these unexploded ordnance contaminated sites can still be carried out, with the active participation of CF specialists that will ensure the safety of workers while the site characterization is on-going.

#### 6.0 CONCLUSION

The ultimate goal of site characterization is to provide effective and sufficient information to assess environmental risks and to allow a decision-making process for the development of an optimal remediation plan. The characterization of contaminated ranges must include all aspects of a standard characterization plan, such as quality assurance and a quality control program. However, explosives are just now gaining recognition as possible sources of soil or groundwater contamination. Therefore, specific actions for the effective and safe characterization of explosive contaminated sites must be taken. This report will be used as a reference to allow the effective characterization of these sites by taking into account the safety, limitations and advantages of the known techniques and their cost.

The best approach to assess the environmental impact contamination by explosives is to begin with a hydrogeological characterization of the site. The reason why this approach is recommended is that most ranges consist of very large areas. To complete an extensive soil characterization of these areas would be extremely costly. The screening of groundwater up and down gradient of the site will provide the first indication of whether or not there is an environmental impact. Wells should be installed at the range with the participation of a hydrogeologist. The first step is to evaluate the potential of finding unexploded ordnance on the range and, if yes, no well should be drilled without proper clearance and specific precautions (level-3 clearance). This groundwater sampling will indicate if the leaching of explosives and explosive metabolites have contaminated

the watertable. At the same time, random composite soil samples may be taken to get preliminary results. If there is an environmental impact and traces of explosives are detected in the groundwater samples, a more detailed soil sampling plan must be implemented. The soil characterization should then follow the procedures recommended in the Sections 2.1 and 2.2 of this report in order to minimize the large heterogenous pattern demonstrated by explosives. Subsurface sampling on the range should be conducted when ever possible based on the history of the site and the probability of finding unexploded ordnance buried in the soil.

Field screening methods should be used in many situations in order to decrease the risk and cost associated with sampling. The most useful application of field screening methods are:

- the establishment of safety levels for the manipulation of highly potentially contaminated samples in relation with the 10% threshold safety limit: colorimetric test recommended.
- the screening of soil or water samples for the absence/presence of explosive compounds to determine whether these will or will not be sent to laboratory for HPLC analysis, or for the establishment of the most effective sampling plan to delineate the area and depth of contamination of both the soil and groundwater:
  - for TNT- and RDX-contaminated ranges: both field method can be used.
  - for HMX-contaminated range: only the colorimetric method can be used.
  - for the safe disposal of pumped groundwater: both tests are applicable, except for HMX.

The collection, conservation and treatment of the samples should be done according to the recommendations stated in Chapter 2. The extraction and analysis with the HPLC laboratory method should be carried out following the recommendations in Chapter 3. The soils should be extracted in accordance with the standard sonication method, while water extraction should be done using the SPE and SPME methods. The other techniques described, such as ACE or SPME, might be used in specific cases. All the aspects related with the environmental impact fate and soil/explosive interactions, as described in Chapter 4 should be integrated in the sampling strategy. Finally, the specific chemical and physical properties of an explosive must be taken into consideration and the safety precautions outlined in Chapter 5 should be carefully followed.

The main conclusion of this report is that certain CF activities may lead to the accumulation of explosives in the environment. From the experience gained in sampling various DND ranges, we were able to ascertain that the extent of this problem is limited in Canada compared with other countries. Most DND ranges that DREV has characterized up to now have limited or no explosive contamination or low levels of multicontamination. However, some sites may still contain high levels of explosive residues, such as the sites where many dud fired munitions are present. From our experience, we were able to establish that no DND ranges will be above the 10% threshold limit concentration of explosives in soil. However, lower levels of explosives can still represent a threat to human health and to the surrounding environment; thus, the screening of potentially contaminated ranges should be conducted.

The goal of this characterization work was not to stop any of the operational activities of the CF. It was rather carried out to assess the environmental impact of these activities, so that proper remedial action and safety precautions could be taken in operations at ranges. Recommendations could be drafted in order to pursue these activities, while minimizing their environmental impact. In conclusion, all the literature covered and the collaborative R&D work described in this report will help the CF to pursue its activities in an environmentally responsive manner. It will also place the CF

in an international leadership role towards the environmental assessment of explosive handling activities. Another R&D program conducted at DREV was devoted towards the development of remediation technologies that may be used to clean up explosive contaminated soils. Both aspects of R&D related to the characterization and remediation of soil contaminated with explosives put DND in a readiness state for any future needs.

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TABLE IPhysical and chemical properties of nitroaromatics and nitramines

Analyte	Molecular Weight (%/mole)	Melting Pt (°C)	Boiling Pt (°C)	Water Solubility (mg/L)	Vapour Pressure at 20°C/torr
TNT	227.13	80.1-81.6	240 (explodes)	130 @ 20°	1.1 X 10 <sup>-6</sup>
RDX	222.26	204.1	(decomposes)	42 @ 20°	4.2 X 10 <sup>-9</sup>
HMX	296.16	276-280	(decomposes)	5.0 @ 25°	3.3 X 10 <sup>-14</sup>
TNB	213.11	122.5	315	34 @ 20°	2.2 X 10 <sup>-14</sup>
DNB	168.11	89.6	300-303	460 @ 15°	3.9 X 10 <sup>-3</sup>
Tetryl	287.14	129.5	(decomposes)	80	5.7 X 10 <sup>-9</sup> @ 25
2,4-DNT	182.15	70	300 (decomposes)	270 @ 22°	2.2 X 10 <sup>-4</sup> @ 25°
2,6-DNT	182.15	64-66		206 @ 25°	5.67 X 10 <sup>-4</sup>
2-A-DNT	197.17	176		2800	4 X 10 <sup>-5</sup>
4-A-DNT	197.17	171		2800	2 X 10 <sup>-5</sup>

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TABLE II

Frequency of detection of explosives residues  
in soil samples analysed at various sites using Method 8330

	<b>TOTAL</b>
Installations	46
Samples analyzed	1155
Samples with detectable explosives	319
<b>Analytes detected</b>	
HMX	37
RDX	87
1,3,5-TNB	108
1,3-DNB	53
Tetryl	28
NB	0
TNT	209
4-Am-DNT	21
2-Am-DNT	54
2,6-DNT	23
2,4-DNT	143
2-NT	0
3-NT	0
4-NT	0

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TABLE IIIDetection limits colorimetric method

Compounds	Minimum Sensitivity (ppm)*
2,4,6-trinitrotoluene	1
2,4-dinitrotoluene	0.5
2,6-dinitrotoluene	2.1
2-nitrotoluene	>100
3-nitrotoluene	>100
4-nitrotoluene	>100
4-amino-2,6-dinitrotoluene	>100
1,3,5-trinitrobenzene	0.5
nitrobenzene	>100
tetryl	0.9
1,3-dinitrobenzene	ca. 0.5
RDX/HMX	0.8

\* The lowest concentration at which the analyte is distinguishable from a matrix blank by two standard deviations

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TABLE IVMaximum holding time (MHT) for nitroaromatics and nitramines

Target analyte	MHT Water (4°C)	MHT Water (-20°C)	MHT Soil (4°C)	MHT Soil (-20°C)
Nitroaromatics	28 days*	6 months	7 days	8 weeks
Nitramines	50 days	6 months	8 weeks	6 months

\* (Stabilized with NaHSO<sub>4</sub>, 1.5g/L)TABLE VPercentage recovery from spiked soil at the 3 mg/kg level using ASE technique

Sample	HMX mg/kg	RDX mg/kg	TNT mg/kg	DNT mg/kg
1	3.07	3.06	3.03	3.14
2	2.99	2.89	3.02	3.07
3	2.99	2.86	2.92	3.06
4	2.84	2.74	2.81	2.97
Average	2.97	2.89	2.95	3.06
Recovery (%)	99.0	96.3	98.3	102
RSD (%)	3.2	4.6	3.5	2.3

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TABLE VIDetection limits using HPLC-EPA 8330

	mg/kg
HMX	1
RDX	1
1,3,5-Trinitrobenzene (TNB)	0.3
1,3-Dinitrobenzene (DNB)	0.3
Tetryl	0.7
Nitrobenzene (NB)	0.3
2,4,6-Trinitrotoluene (TNT)	0.3
2-Am-Dinitrotoluene (2-Am-DNT)	0.3
4-Am-Dinitrotoluene (4-Am-DNT)	0.3
2,6-Dinitrotoluene (2,6-DNT)	0.3
2,4-Dinitrotoluene (2,4-DNT)	0.3
2-Nitrotoluene (2-NT)	0.3
4-Nitrotoluene (4-NT)	0.3
3-Nitrotoluene (3-NT)	0.3

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TABLE VIIDrinking water criteria for munitions-related chemicals

Compounds	Criteria (ppb-ug/L)
TNT	1.0
RDX	2.0
HMX	400
2,4-DNT	5.0
2,6-DNT	5.0
1,3,5-TNB	1.0

TABLE VIIIHuman health risk based criteria in soils for RDX, TNT and HMX

Compounds	Criteria (Daniels) mg/K	Criteria (Rouisse) mg/Kg
TNT	0.3	0.024
RDX	0.3	0.00012
HMX	1.7	2.2

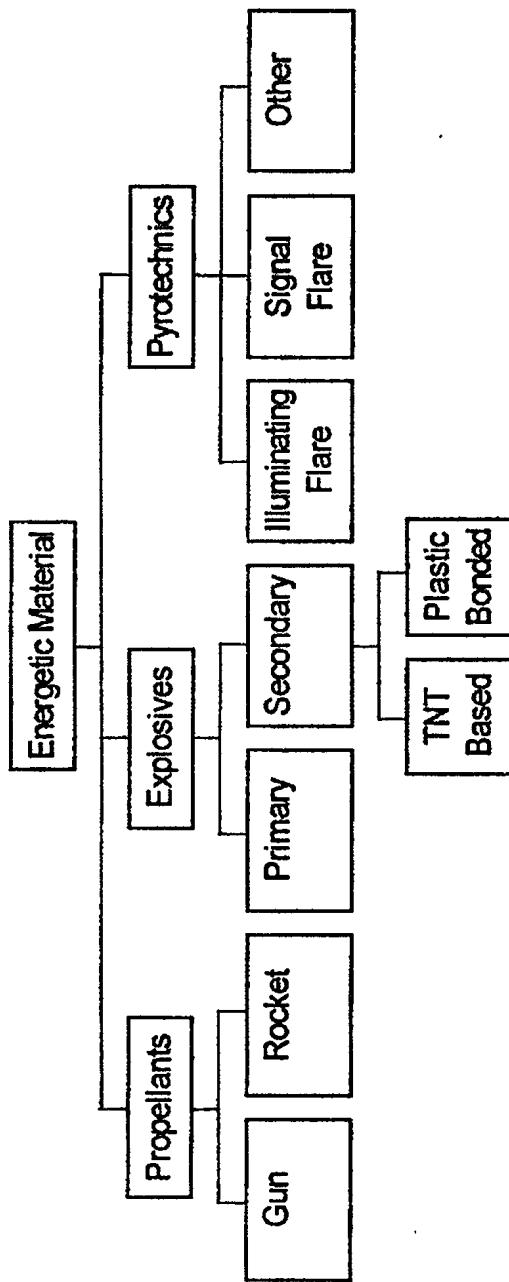


Figure 1 - Categories of energetic materials

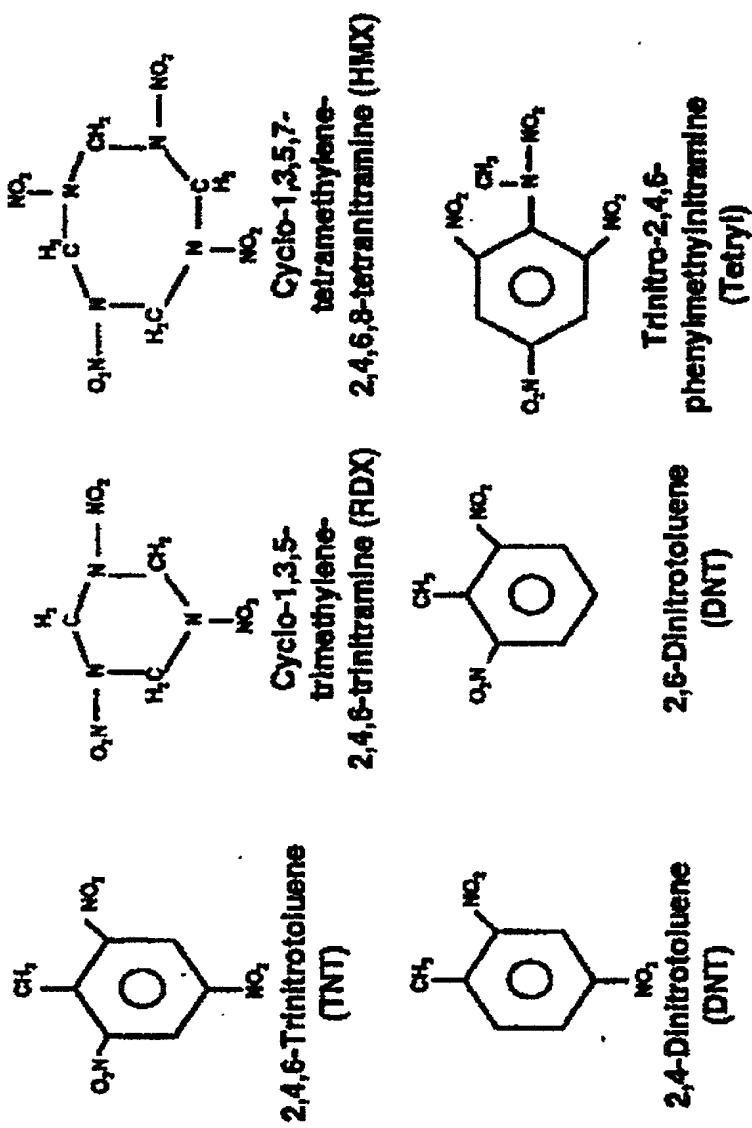


Figure 2 - Chemical structures of common explosive compounds

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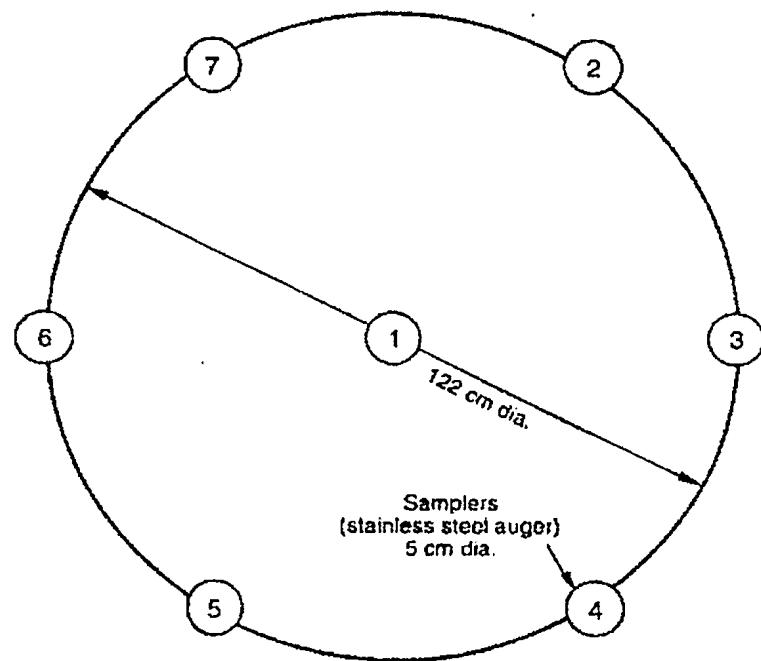


Figure 3 - Circular pattern for discrete samples collection

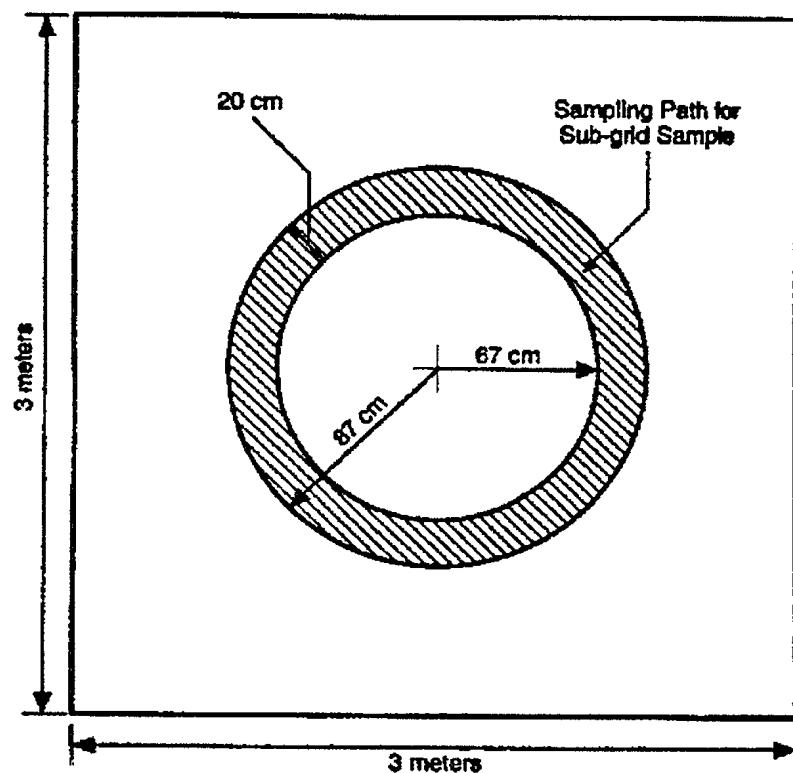


Figure 4 - Sampling path: Area integrated samples

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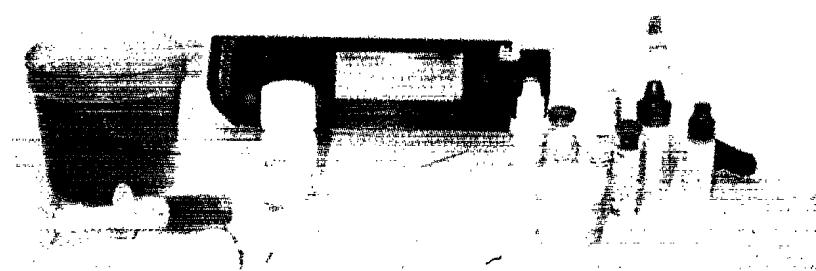


Figure 5 - Enzyme immunoassay field test

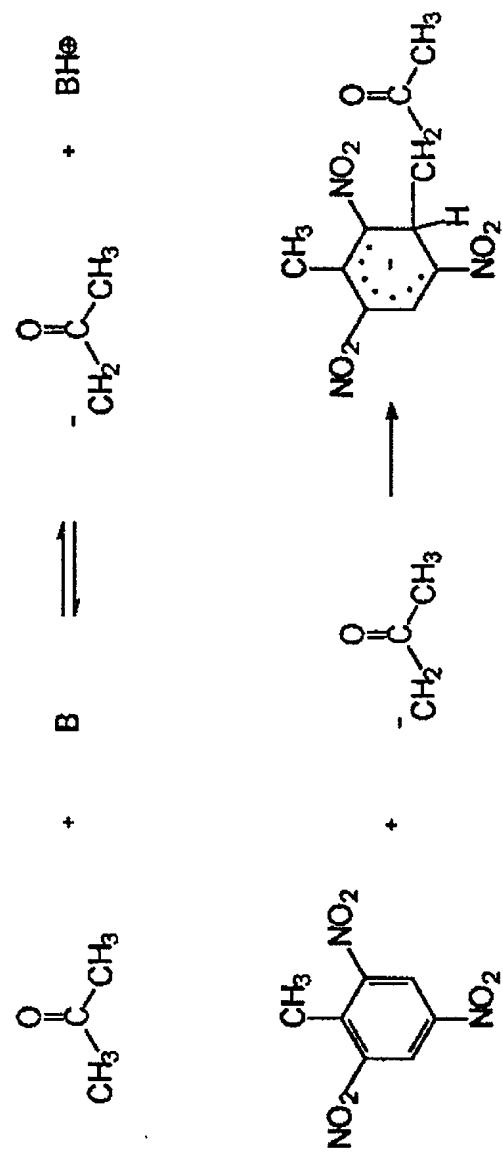


Figure 6 - Janosky reaction

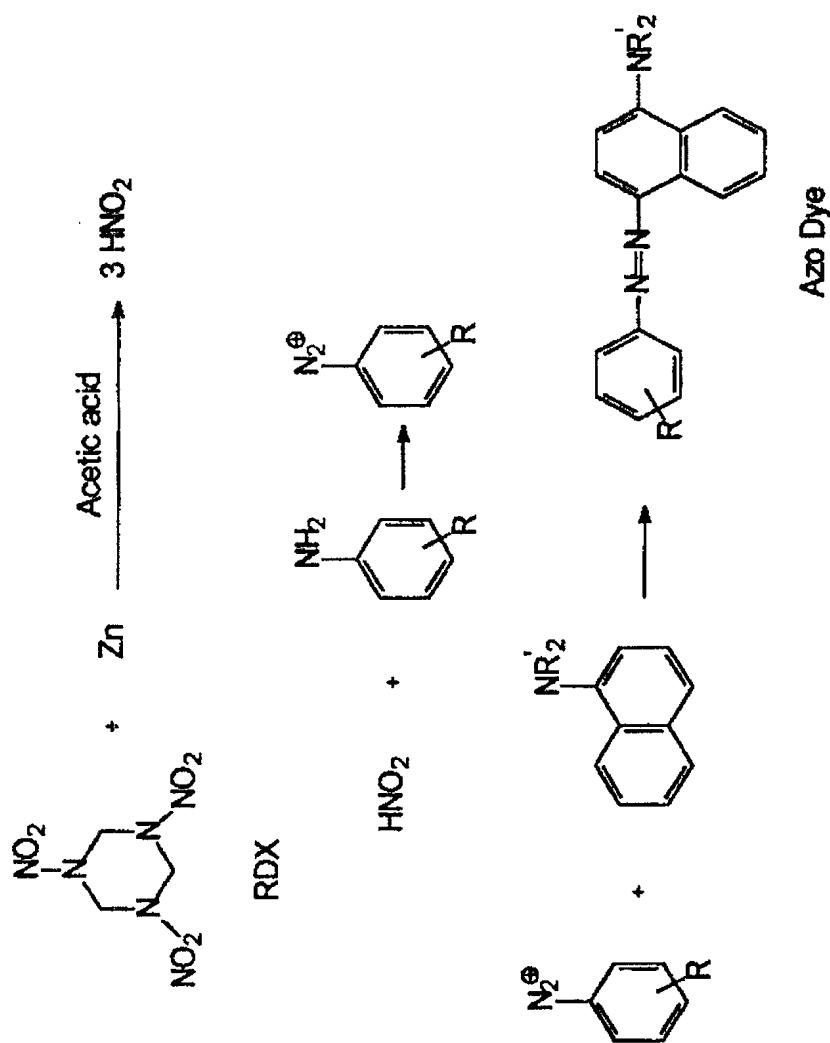


Figure 7 - Griess reaction

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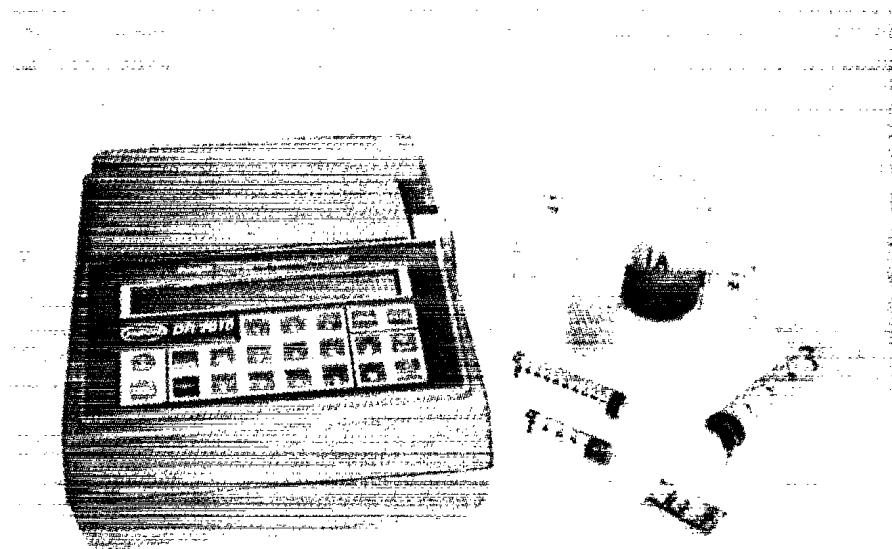


Figure 8 - Colorimetric field screening method

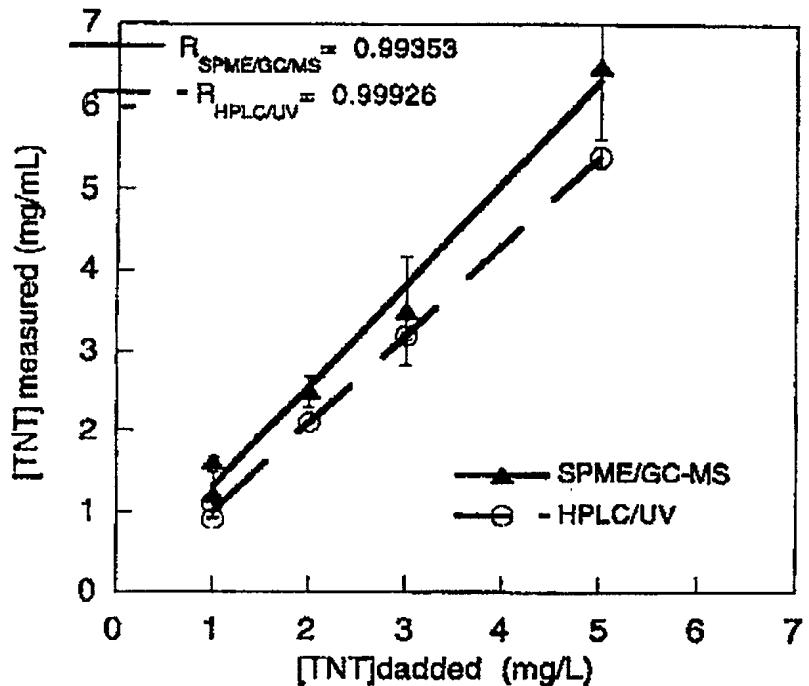


Figure 9 - Concentrations of TNT in artificially contaminated water: SPME/GC-MS versus HPLC/UV (EPA # 8330). Error bars were based on triplicate measurements (DL 9 ppb).

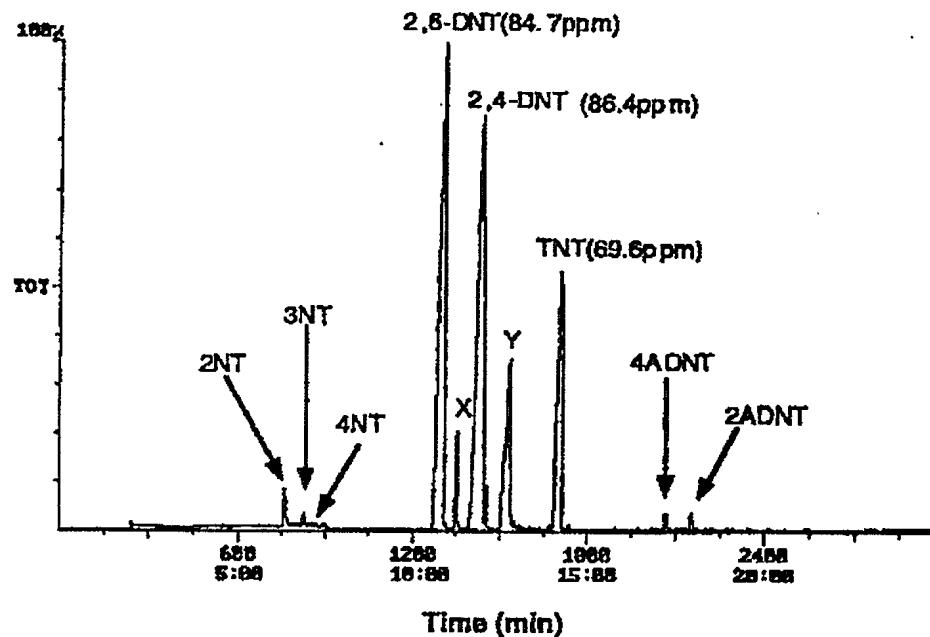


Figure 10 - SPME/GC-MS total ion chromatogram obtained from a ground water sample taken from a contaminated site

(GC conditions: a DB-5 column (30m X 0.2mm ID 0.25 um film thickness) Helium as the carrier gas, initial T 90°C for 2 min. increased to 165°C at a rate of 10°C/min. followed by a rate increase of 5°C/min until 250°C).

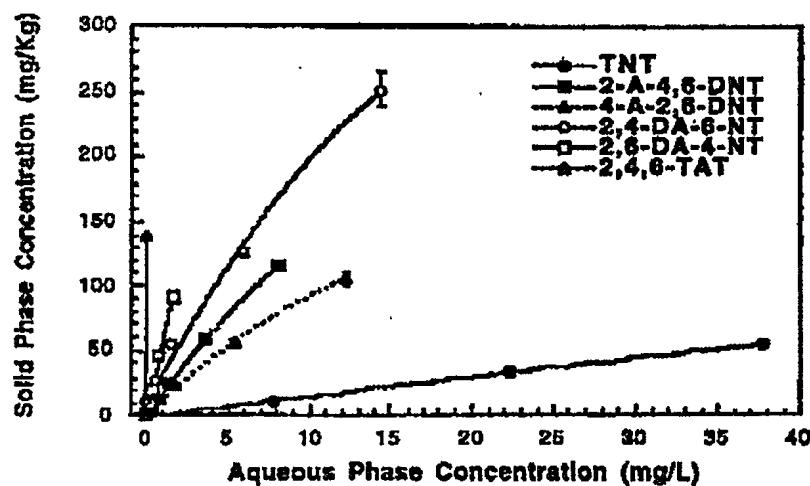


Figure 11 - Adsorption isotherms of TNT and metabolites in top soil

(84% sand, 12% silt, 4% clay, 8.4% organic matter). Soil/water mixtures were shaken for 16h (1h for TAT) and centrifuged. The analyte concentration in the aqueous phase were determined by HPLC (EPA method 8330) and those in soil were determined by difference.

A non-linear form of Freundlich equation  $Q=K_d C^N$  was followed where  $Q$  is TNT adsorbed per gram of soil,  $K_d$  is the distribution coefficient of the contaminant between the soil and liquid phases,  $C$  is the equilibrium concentration of TNT in the liquid phase, and  $N$  is a constant.

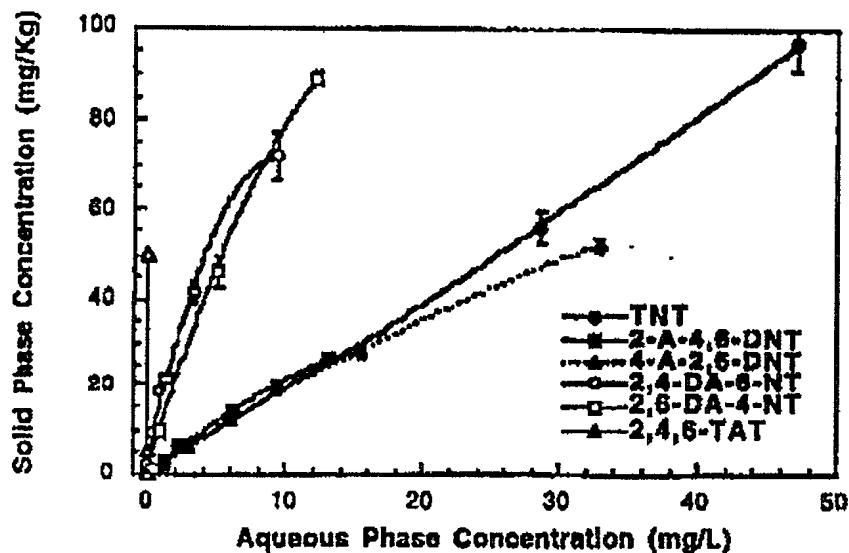


Figure 12 - Desorption isotherms of TNT and metabolites in water

For the desorption study, fresh distilled water containing no analyte was added to the same soil used in the adsorption study (Figure 11).



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<b>11. ACCÈS AU DOCUMENT</b> (Toutes les restrictions concernant une diffusion plus ample du document, autres que celles inhérentes à la cote de sécurité.)  <input checked="" type="checkbox"/> Diffusion illimitée <input type="checkbox"/> Diffusion limitée aux entrepreneurs des pays suivants (spécifier) <input type="checkbox"/> Diffusion limitée aux entrepreneurs canadiens (avec une justification) <input type="checkbox"/> Diffusion limitée aux organismes gouvernementaux (avec une justification) <input type="checkbox"/> Diffusion limitée aux ministères de la défense <input type="checkbox"/> Autres (préciser) :				
<b>12. ANNONCE DU DOCUMENT</b> (Toutes les restrictions à l'annonce bibliographique de ce document. Cela correspond, en principe, aux données d'accès au document (11). Lorsqu'une diffusion supplémentaire (à d'autres organismes que ceux précisés à la case 11) est possible, on pourra élargir le cercle de diffusion de l'annonce.)				

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13. **SOMMAIRE** (Un résumé clair et concis du document. Les renseignements peuvent aussi figurer ailleurs dans le document. Il est souhaitable que le sommaire des documents classifiés soit non classifié. Il faut inscrire au commencement de chaque paragraphe du sommaire la cote de sécurité applicable aux renseignements qui s'y trouvent, à moins que le document lui-même soit non classifié. Se servir des lettres suivantes: (S), (C), (R) ou (NC). Il n'est pas nécessaire de fournir ici des sommaires dans les deux langues officielles à moins que le document soit bilingue.)

Many activities of the Canadian Forces such as firing, demolition practices and destruction of obsolete ammunition by open burning and open detonation may lead to the spreading of energetic compounds in the environment. These compounds are being closely examined due to their highly specific physical, chemical and toxicological properties. In Canada, limited effort has been spent to examine this particular environmental threat. In this context, R&D was dedicated towards the establishment of a protocol that will allow reliable and safe characterization of sites potentially contaminated with explosives. The protocol detailed in the present report covers all aspects related to surface and sub-surface sampling, extraction, analysis, field screening methods and environmental fate related with these specific contaminants. Furthermore, safety procedures are described that take into account the explosive and toxic nature of these compounds. This report will serve as a reference guide for any future sampling campaigns on potentially explosives contaminated sites.

14. **MOTS-CLÉS, DESCRIPTEURS OU RENSEIGNEMENTS SPÉCIAUX** (Expressions ou mots significatifs du point de vue technique, qui caractérisent un document et peuvent aider à le cataloguer. Il faut choisir des termes qui n'exigent pas de cote de sécurité. Des renseignements tels que le modèle de l'équipement, la marque de fabrique, le nom de code du projet militaire, la situation géographique, peuvent servir de mots-clés. Si possible, on doit choisir des mots-clés d'un thésaurus, par exemple le "Thesaurus of Engineering and Scientific Terms (TESTS)". Nommer ce thésaurus. Si l'on ne peut pas trouver de termes non classifiés, il faut indiquer la classification de chaque terme comme on le fait avec le titre.)

SITE CHARACTERIZATION

TNT

RDX

HMX

ANALYTICAL CHEMISTRY

HETEROGENEITY

SAMPLING

FIELD SCREENING METHODS

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